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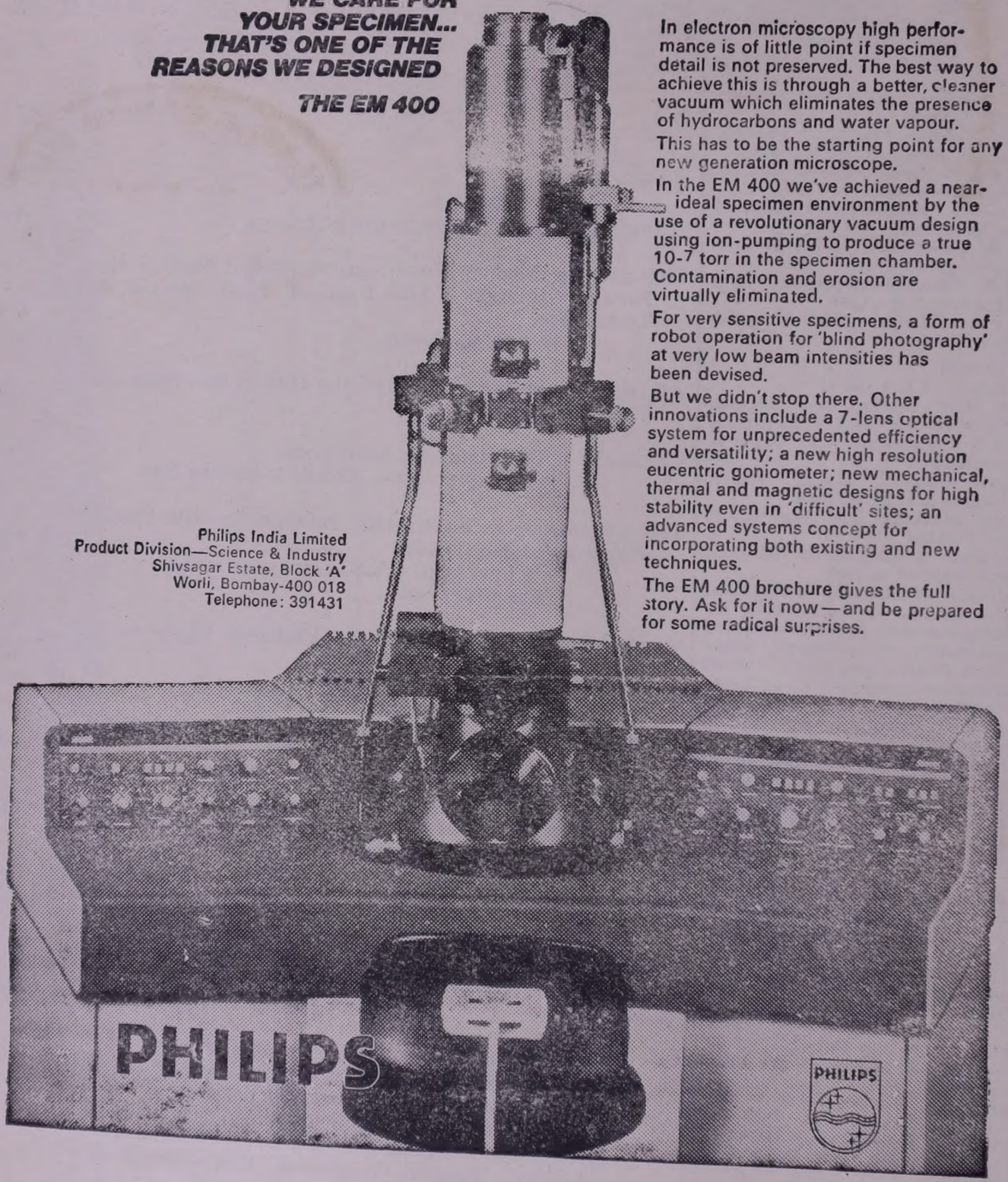

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Current Topics

Sun : Mankind's Future Source of Energy

AN inevitable consequence of the ever-increasing pace of industrialization all over the world during the past few decades has been the recognition of the importance of energy as a highly strategic and vital resource. During the last two hundred years, new sources of energy have appeared on the scene at intervals of approximately 50 years. But every new energy source — coal, gas, oil, hydel and nuclear energy—has been supplementing, rather than replacing, the older ones. The situation is going to be different in the years to come. Most of these resources are non-renewable and their reserves will start getting exhausted over periods ranging from 30 to 100 years. Other disadvantages of these resources are their uneven distribution (responsible for situations like the recent 'enrgy crisis') and the environmental hazards associated with their use. Mankind has, therefore, very rightly pinned hopes on sun as the most dependable source of energy for the future. Besides being free from the hazards associated with the conventional sources of energy, it is one source over which every nation and every human being has the same right.

A lot of research has been in progress during the last two decades on various aspects of utilization of solar energy and it was appropriate that 'Sun: Mankind's future source of energy' was chosen as the focal theme for the seventh biennial International Solar Energy Congress (ISEC 77) held in New Delhi during 16-21 January 1978. Organized by the International Solar Energy Society with the collaboration of the Solar Energy Society of India, the Department of Science and Technology, Ministry of Energy, the Council of Scientific and Industrial Research, the Indian Council of Agricultural Research, Bharat Heavy Electricals Ltd, Tata Energy Research Institute, Unseco and the Commonwealth Secretariat, the congress provided an excellent opportunity for exchange of information among workers from different countries, for taking stock of the situation and formulating policies and programmes for solar energy research for the future. The congress, held for the first time in a developing country, brought together over one thousand experts from about 60 countries. The main topics of discussion at the technical sessions at which about 400 papers were presented were: (1) International and national plans and programmes; economic aspects, policy, social and implementation aspects; (2) Solar radiation; energy storage; photovoltaics; photochemistry, photobiology; and biomass; (3) Flat plate collectors, including solar ponds and selective surfaces, concentrating systems; (4) Space heating and cooling, including water and swimming pool heating; solar energy and architecture; solar thermal power systems; wind power; and (5) Agricultural and industrial applications, including distillation.

The information presented by experts at the technical sessions as well as the working and other models displayed at the exhibition held at the time of the congress provided ample evidence that a lot of ground has already been covered in solving various problems encountered in making commercial utilization of solar energy technically feasible and economically competitive with the conventional energy sources. It was evident that solar energy is moving from the stage of research and development to field trials. Substantial advances in the harnessing of solar energy have been made in USA, Australia, Canada, Israel and Japan. In the next 15 years, 13 million houses in USA are proposed to be equipped for solar heating. This alone will entail saving in energy value equivalent to 30 million tonnes of coal. The first phase of the solar thermal energy conversion programme in USA scheduled to become operational is the 5 kW facility being built at Sandia laboratories. In India, the work has so far been mostly in the field of low grade thermal processes, such as solar water heating, solar distillation, solar drying, pumping, space heating and solar cooking. Indigenous design and technology for the manufacture of flat plate collectors have been developed and standardization and optimization of collectors for specific applications are being carried out. The Department of Science and Technology has funded about 25 research and development projects and Rs 10 million have been allocated in the current year for solar energy research. Priority has been given to projects of particular relevance to rural development, such as (1) development of solar water pumps of 2-5 hp capacity for irrigation purposes; (ii) solar mini-power plant for rural applications; (iii) cold storage for food preservation; (iv) solar distillation and desalination; and (v) solar drying.

India is fortunate that the total solar insolation falling on one square metre surface, horizontal to the sun, is higher than in many countries in the tropical and temperate zones. Therefore, there is obvious need for according top priority to research and developmental projects concerning commercial utilization of solar energy. She can ill-afford to lag in this vital area.

Strategies for Meeting Food and Nutritional Need of the Rural Population—The Roles of Food Science & Technology

NARENDRA SINGH
Protein Technology Discipline, Central Food Technological Research Institute, Mysore 570 013

THE above seminar, organized by the Association of Food Scientists and Technologists (AFST) Southern Region Branch, was held in Madras during 23-24 April 1977. The associate organizers were the Tamil Nadu Agro-Industries Corporation, Department of Agriculture of the Government of Tamil Nadu and the Food Corporation of India.

The inaugural session on 23 April was followed by four technical sessions on (1) Nutritional needs of the rural population and means of fulfilling them; (2) Appropriate technologies for food processing in rural areas; (3) Some case studies; and (4) Constraints in setting up food processing units in rural areas and evolving food and nutrition policy and planning. The recommendations emanating from different technical sessions were discussed at the final plenary session.

Inaugural Session

The AFST President, M.R. Chandrasekhara, in his welcome address, said that as an extension of the 1976 Science Congress Session and the COSTED meeting in March 1977 in Madras, dealing with the general theme of rural development and science and technology, the present seminar was concerned with the specific problems of food and nutrition in rural areas.

Presiding over the session, B.L. Amla (Director, CFTRI), cautioned that there was a need to take into account the sociological conditions and other problems during the transfer of technology culture to the rural areas, and emphasized that there should be less sophistication and low capital in such technology transfers.

The seminar was inaugurated by P. Govindan Nair, Acting Governor and Chief Justice of Tamil Nadu. He made three main points: (1) In India, 80% population was rural and the producer of food for all, but the same people were also victims of malnutrition, ill health and poverty, and the children the worst sufferers. (2) Low productivity of agriculture, its uneven development and dependence on vagaries of nature, needed to be overcome with the help of science and technology, but with attention to a rational use of the available resources of land and water. (3) The main reason for under-development in rural areas was poverty, creating need for the development of both agricultural and non-agricultural sectors. For overcoming the problem of ill health, provision of sufficient food alone was not enough; equally necessary were improvements in eating practices, methods of cooking, etc. He hoped that the seminar would suggest suitable strategies and spell out the role of food scientists and technologists in improving the health of rural people and in eradicating poverty and making them stronger and healthier, so that they can make a bigger contribution to food production.

V. Subrahmanyan, the doyen of food science and technology in India, delivered the keynote address "A realistic approach to problems of rural areas in relation to nutrition." He focussed attention mainly on the following points:

(1) The most important point was a reference to an intensely agricultural district like Thanjavur, the gross earnings of which were Rs 200 crores/annum from its local labour and other resources. However, from the gross, the net earning of Rs 15-20 crores was not being invested locally but taken out to urban areas and other regions. The area producing this wealth and profit remained in almost the same poor condition as it was several decades back—old houses and more huts with mud walls and thatched roofs. In the past, though low-paid, the majority of people had some rice to eat, but no longer now. Over these years has continued the process of migration of enterprise and talent, with the poor and dull majority staying on, according to him.

(2) Lack of improvement in the living conditions in India over the last 6-7 decades, despite the increase in land under cultivation, and also in yields of foodgrains, is accompanied by the following: (a) Population increase and the deteriorating economic conditions to further worsen unless checked by a miracle of agricultural or industrial revolution; (b) uneven development, exclusive dependence on agriculture, its seasonal occupational character, causing heavy rural indebtedness, combined with general poverty and wasteful customs, which are promoting corruption and other evils; and (c) low production of nutritious foods as a consequence of efforts to get something out of almost nothing, a typical example being that of improved breeds of dairy cows not given adequate feed, resulting in worsening yields.

(3) The steps suggested for increasing the production of nutritious foods included the following: (a) Need for trials with new approaches like permanent grasslands on arable areas in the villages, promotion of mixed farming of crop and animal husbandry, promotion of marine and inland fishing, and also more attention to meat production, as majority of the people are non-vegetarians; (b) processed foods for better nutrition to be developed and promoted on consumer preferences, not on low income tests and nutritive value but with examples from the experimenters' personal family use, and association of medical practitioners; (c) production of edible rice

bran oil, and utilization of rice germ; (d) more emphasis on tuber crops—tapioca, sweet potato with extension in delta areas, better and simple storage and evolution of new varieties; (e) diversion of millets and other coarse foodgrains for sharing with animals for increasing food production; (f) greater attention to pulses in respect of yields and marketing; and (g) greater attention to soybean and coconut for oil.

(4) Drawing attention to the time lag of 10-15 years in research findings and their application, the difficulties were enumerated as insufficient pilot studies, inadequate understanding of the requirements of the consumer, the administrator's bureaucratic approach, and the exaggerated targets fixed by the politicians.

Nutritional Needs of the Rural Population and Means for Fulfilling Them

Rajammal P. Devadas (Sri Avinashilingam Home Science College, Coimbatore) surveyed the nutrition problems of the rural population and suggested the following strategies: Change in economic and social structure of the nation, augmentation of food production, adoption of proper methods of processing and storage, equitable food distribution, nutrition education and extension, introduction of supplementary feeding programmes and improvement of environmental sanitation.

S. Rajagopalan (Nutrition Project of Government of India in Tamil Nadu) enunciated the basis of nutrition policy as fulfilling the legitimate aspirations for the basic needs of life, equitable distribution of benefits of social and economic development, and consistency in, and mutual reinforcement of, policies at different levels. In respect of the policies relating to food supplies, he stressed the need for balanced production of all the needed foods within the country and, for that purpose, a comprehensive price policy to influence crop patterns. On the policies relating to distribution, he pointed to poverty as the single factor, and called for effective measures to reduce income inequality. He also urged the need for understanding the nutritional consequences of the various policies currently in operation in the country.

G.P. Ranganathan (Union Ministry of Food, Madras) called for support to the "save grain campaign" and to strengthen it through apt training and demonstration programmes. He suggested adoption of villages for provision of modern storage structures and improvement in the existing facilities.

D. Srinivasa (Mysore Snack Foods, Bangalore), highlighted the experiences gained from a Ready-to-Eat Extruded Food Mid-day Meal Programme. This was a totally state assisted programme for primary school children (6-11 years). It started on 1 November 1975 with 30,000 children, and later in January 1976 covered about 42,000 in the Bangalore (urban and rural) and Kolar districts. According to him, there was spontaneous acceptance of the food and the programme by children, teachers and administrators.

S. Neelakantan (Tamil Nadu Agricultural University, Coimbatore) drew attention to the importance of nutrition education of school going children and also of adults, particularly the mothers, and of education for better food practices and to the role of village workers and doctors.

K.V. Palanidurai (Tamil Nadu Planning Department) described the status of nutrition in Tamil Nadu. He showed that there was very low per capita consumption of foods other than cereals; that 46% rural and 37·3% urban population were below the nutritional poverty line (a total of 17 million in 1969-70); and that 87% of rural population could not spend more than Re 1.00 per day on food. Later, he described the perspective of the Tamil Nadu nutrition programmes. By 1985, this plan, with a total outlay of Rs 203 crores, was to cover 7·5 lakh children in 12,500 balwadis and also preschool children, and expectant and nursing mothers. Its essential ingredients were the use of local foods and health care.

G. Rama Rao presented the costing and other details of the Energy Food of CFTRI prepared for the India Population Project in Karnataka.

During discussion, the following three points were enunciated to form the basis for nutrition policy:

(1) The economic conditions, purchasing capacity and poverty, as the most important factors, are accepted by all, but in practice these are ignored and emphasis is laid on other points. Hence, a clear enunciation of the fact that eradication of poverty is the only solution is necessary; the other measures are transitional and appropriate only during exigencies like famine, draught and earthquake.

(2) Welfare feeding programmes serve no useful purpose, except propagation of benevolence, and are associated with inherent malpractices. However, since they are continuing, they must be made independent of foreign agencies/assistance, and made totally dependent on local resources of materials and capital and management, and the foods must not only be based on traditional raw materials but also be traditional and simple, involving no processing and distribution from outside.

(3) The nutritional problem is of a serious nature and, therefore, must be treated on war footing. Besides attack on poverty, equitable distribution of foods, specially the protective foods like pulses, milk, oil/ghee/butter, at cheap and subsidised rates to families below the poverty line, must be given top priority, and statutory measures should be adopted for this purpose.

Appropriate Technologies for Food Processing in Rural Areas

V. Sankaran highlighted the achievements of the Tamil Nadu Agro-Industries Corporation (TNAIC). He referred to the plants already in operation like the Modern Sunflower Oil Milling Factory, the Macaroni Plant based on wheat suji, and the Maize Products Plant, yielding suji, flour and bran. He also mentioned the proposal for a fruit processing plant.

R. Srinivasan (Tamil Nadu Directorate of Fisheries) talked about the Fish Farmers Development Agency in Thanjavur District. According to him, there has been a decrease in the production and consumption of dried and salted fish and also in the consumption

of fresh fish, while there has been an increase in the production of frozen and canned fish. Currently, the latter is almost entirely exported. He drew attention to the great losses in the modern practice of fishing and in shrimp fishing; the full catches are not brought inland, the trash fish and fishes other than shrimp being discarded in the sea itself. He called for the adoption of modern fish preservation methods and artificial dryers and processing of fish flour and other products in rural areas.

A.K. Govil (Dandekar Machine Works) made a plea for an integrated "Field to food" approach, i.e. greater yields of paddy giving higher processing yields of rice. He argued for parboiling for improving both yield and nutrition. While suggesting the adoption of modern engineering techniques in rice milling and parboiling, he wanted action to discourage proliferation of milling equipment manufacturers and, instead, asked for a few modern monopoly mills.

R.N. Datta (Food & Nutrition Board, Govt. of India, Madras) presented feasibility reports on the setting up of rural food processing units for the production of 1-1.5 tonnes/day products for feeding programmes.

During the discussion, the following points emerged: (1) Rural industrial development may be possible only if (i) along with employment, capital is generated and locally reinvested; and (ii) the production is of consumer goods for local markets and not of goods for export; (2) Supplementary foods do not form part of the production economy and only such foods be used in these programmes which are available in the market; (3) Conservation of fruits and vegetables is the most important technological approach, and in this context the question of reusable bottles needs to be looked into seriously. It was suggested that regional production mainly for local and regional markets should be promoted. This is one way how manufacturers can manage and arrange to keep the reusable bottles in circulation. The location of industries not only close to raw materials, but also to the markets, is complementary to reusable bottle/container approach and also necessary for successful industrial development.

Case Studies

S.V. Pingle (Food Corporation of India) opened the session with the remarks that there were now very large stocks of foodgrains in government hands and their liquidation was an important issue.

M. Srikrishna presented a case study of Tamil Nadu Dairy Development Corporation (TNDDC) project. Under it, Rs 12 lakh were distributed as the first loan among 600 members of cooperative societies of Harijan families who were willing to maintain one or two animals. The milk was collected by the corporation twice daily. Nearly 80% of the farmers have repaid the first loan and drawn even the second loan. An expansion was planned to cover 1500 additional farmers. It was stated that half of the milk was left with the farmers for their consumption.

G. Kamalanthan (Sri Avinashilingam Home Science College, Coimbatore) described the success of an applied nutrition programme in which *laddus* prepared incorporating leaf protein were found very popular.

T.N. Murthy (CARE Food Technologist, Hyderabad) presented information on a ready-to-eat processed food factory sponsored by the Andhra Pradesh Child Nutrition Council. This was expected to produce 20 tonnes of fried noodles (*sev*), an extruded product based on imported PL-480 commodity of CSM; under this programme several hundred thousand beneficiaries were to be covered.

J.V. Shankar (CFTRI, Mysore) presented his analysis of the socio-economic and resource data on two villages, available in a survey report prepared by the students of Mysore Administrative Training Institute. He identified four areas which deserved increased inputs as family income through agriculture and industries, education, health and welfare, and nutrition.

N. Subramanian (CFTRI, Mysore) discussed the Karimnagar Project of the CSIR. From the details provided it was clear that the benefits were going only to the few rich in the area.

H.V. Butt described the Chevella experiment of the "Indo-Dutch Project" in the Andhra Pradesh. Started in 1970, this was a comprehensive programme of education, health and nutrition, covering a population of about 46,000 in 47 villages. The programme was reported to be quite successful, but for some technical problems of storage and packaging of the food.

V.H. Potty (CFTRI, Mysore) presented details of a proposal for the manufacture of mutually supplemented mixes for 6-20 month old children.

During discussion, among others, a few questions on the acceptability of leaf protein and on its low level incorporation were raised. In reply, the CFTRI experience on favourable acceptance of green protein was narrated and it was explained that the level of incorporation would correspond to the objectives, whether it was meant for supply of pigments, lysine and/or protein. Further, exposing the fallacy of cheap protein for the poor, the present CFTRI approach was explained on the integrated production of green leaf protein for poultry feed and pressed residue for use as cattle fodder.

Constraints in Setting up Food Processing Units in Rural Areas and Evolving Food and Nutrition Policy and Planning

The Indian Standards Institution approach of quality control and its standards covering different foods were described in one paper.

R. Pitchumani [Small Industries Service Institute (SISI), Madras] enumerated the constraints as the lack of rural base, inadequate surplus, storage and other post-harvest problems, and inadequate use of solar energy. As solutions, he suggested the setting up of information centres, promotion of extention and educational efforts, proper coordination of activities and a serious review of the incentives and their consequences.

S. Vaidyanathan described the functioning of the State Industries Promotion Corporation of Tamil Nadu (SIPCOT). Its activities were in the form of

incentive schemes, growth centres, infrastructural formalities, term loans and underwriting assistance and ancillary services.

Narendra Singh (CFTRI, Mysore) discussed some basic concepts on food and other industries for rural areas. While lauding the achievements of the Indian food science and technology, he drew attention to the domination of ruling economic interests in determining the practical developments. This approach led to food industries under monopolies or in the foreign capital/technical collaboration sector, and to the production, not of mass-consumer products, but of goods for affluent and export markets. He pleaded for understanding the origin of poverty in rural areas instead of transplanting approaches from the alienated centres of expertise. He emphasized the importance of industrial development for employment and capital generation with the latter's local reinvestment, for a technology self-reliant on local resources of skill, materials and small capital, and for production of mass consumption goods with a check on their export without satisfying the local needs.

During the discussion, a plea was made to reorient the export policies to promote domestic consumption and accelerate local food production. It was stated that the blame must not be put on the private interest alone, as the government itself was very much a part to the export bias in practice. The FCI expert argued that the government had no alternative but to export when surplus stocks were there, as was at present the case with wheat. He discussed the difficulties in the way of local use of rice bran. Others with practical experience explained that the deoiled rice bran was not acceptable to the dairy producers.

For liquidating the overflowing stocks which are likely to get damaged due to bad storage, a suggestion was made to distribute the excess grain at subsidised rates to the poor people.

On quality aspects, the irrelevance of the ISI standards for Bal-Amul, etc. for rural areas was pointed out. It was also stated that the talk of food and nutrition in rural areas was of no use, a clear solution being an extra Re 1 as the best nutrition for the poor. Therefore, expansion of employment avenues and increase in the remuneration of workers constituted the only fruitful approach.

Final Plenary Session

The most interesting point of this session was a reopening of the argument whether there was any malnutrition in India and, if so, what was its extent. The statement of the expert representing the authority of the Government of India that there was now less malnutrition than 50 years back appeared rather amusing. Presenting no data in support of his assertion, he dealt with the problems of the economics of storage and of subsidised food. Thus, for some time, it become a session of arguments and counter-arguments.

Later, however, there appeared to be a consensus that the problems did exist and that the genesis lay in poverty, the decreasing purchasing capacity and the increasing income disparity. Gravely concerned with the accentuating problems of hunger and malnutrition among the common people, one suggestion was to tackle the same on war footing, with all the necessary measures for ensuring equitable distribution of the vital foods.

The draft recommendations were considered by most participants as mere repetition of what has been stated off and on at other conferences and meetings in the past. Pointing to the term 'rural', someone did question the need for distinction when the rising prices of basic essentials were making difficult all life activities, not food and nutrition alone, and afflicting everyone but the few rich, everywhere in both rural and urban areas. Evidently, this emphasis on 'rural' areas was to fall in line with the new orientations at the international and national levels.

The following recommendations were press-released by the organisers of the seminar:

(1) Maternal nutrition and infant nutrition require priority attention. The nutritional needs of these vulnerable sections of the population living in rural areas required to be met locally. "Mahila Mandal" and village level workers will have to be involved in this endeavour.

(2) The seminar recognized the need for promoting the availability of low cost nutritious foods made out of locally available food materials in the rural areas, to meet the problem of widespread undernutrition and malnutrition.

(3) The subject of food and nutrition, with particular relevance to the rural needs, should form part of the school curriculum all over India as a matter of policy.

(4) The export policy of the country should be reviewed with a view to making available nutritious foods and food byproducts to meet the domestic needs of the population. In this context, export of groundnut cake, rice bran, fruits and vegetables, marine products, etc. required to be reviewed.

(5) Adequate processing facilities should be created to process the above food commodities and make these available to the rural population. This will also help in generating additional rural employment and increasing the purchasing power. In this regard, the seminar felt that labour intensive composite food processing units could easily be set up in rural areas with low investment.

(6) The present foodgrains procurement and pricing policy requires careful examination in order to leave adequate stock of foodgrains with the rural holders throughout the year. Establishment of rural grain banks will help in this regard.

(7) It was realized that the present practices of food storage in rural areas are far from satisfactory. To overcome this, it was recommended that the rural grain storage should be improved, based on modern technology. It was further recommended that simple and scientific storage facilities should be made available in the rural areas.

(8) In view of the recognized advantages of higher yield, lesser breakages and important nutritional contents, it was recommended that parboiling of paddy needs to be popularized on a wider scale. Improved parboiling techniques have already been developed by various institutions to yield parboiled

rice of acceptable quality. A number of small units should be established in rural areas.

(9) Considering the large potential available to develop fisheries it was felt that preservation of fish in different forms to meet the needs of rural population should be developed. The large quantities of trash fish available during certain seasons could also be converted into fish cake and fish flour.

(10) Professional bodies like the Association of Food Scientists and Technologists, which have adequate know-how and expertise, should be consulted in implementing the recommendations of the seminar.

All India Symposium on Natural and Human Resources and Their Utilization

SPONSORED by the University Grants Commission, New Delhi, and organised by the newly founded School of Biological Sciences of Bhopal University, this two-day meet of leading scientists in the field from all over the country, was held on 28-29 October 1977. Marked by a vigorous interaction of ideas, in a tightly programmed workshop like atmosphere, the symposium brought to surface once again and probably more overtly and effectively, the stark fact that the modern approach to solving a scientific, technological or economic problem has to be but multidisciplinary. There could be no compromise on this issue. Inaugurating the symposium, Dr P.S. Parasai, Director of Agriculture to the Govt. of Madhya Pradesh reviewed the agricultural potential of his State in particular and sounded a note of warning that in view of the well-known saying that forests precede civilizations and deserts follow them, it would be nothing short of calamity to increase our agricultural output by bringing additional area under cultivation; instead, he argued, we should try to augment the yields per unit existing area itself.

Water Resources

With Prof. S.V. Ganapati in the chair, the session on water resources opened with the paper by Dr S.N. Dwivedi from the Central Institute of Fisheries Education, Bombay, in which was pointed out how fish farms and seasonal ponds could provide additional fish production and employment. A most exciting example of an unemployed arts graduate, named Diwakar Reddi, from Andhra Pradesh was cited, who, with an initial investment of six thousand rupees, took on lease, in 1975, two acres of rice fields and converted them into fish nursery ponds and has today a seed farm of about seven acres, making a net annual profit of thirty thousand rupees approximately. India has numerous seasonal ponds which retain water for months together during the year, and extensive back waters, mud-flats and mangroves are all highly productive, but most of them remain unused for fish culture. Dr Brij Gopal, Department of Botany, University of Rajasthan, drew attention to the fact that freshwater resources, constituting a small fraction of the total water resources, on which the mankind depends almost wholly, are currently under great stress on account of various human activities, and the resources are not only getting fast depleted but are being dangerously polluted. It was stressed that detailed ecological investigations would be basic to the understanding of this complex problem and proper management of these resources. The note was amplified by Dr B.N. Desai of the Regional Centre of the National Institute of Oceanography at Versova, and Dr P.V. Dehadrai of the Central Inland Fisheries Research Institute, Barrackpore. Dr G.P. Verma, from the College of Agriculture, Indore dealt extensively with management of water resources under rain-fed farming and pointed out that in Madhya Pradesh, where only 8% of the cultivated area has irrigation facilities, a judicious management of the rainfall water is a must. Dr Verma presented a scheme to let out excess of rain water from fields safely without causing soil erosion, store it in an appropriate manner and then recycle it when needed. Shri P. Sita Rami Reddy from the Centre of Advanced Study in Marine Biology, Annamalai University listed fish resources of Porto Novo waters and stressed that the presence of large numbers of larvae and juveniles of mullets and prawns encountered in the shore, estuarine, backwater and mangrove areas is a clear pointer to the immense potential these water bodies hold for full time aquaculture practices that could be profitably undertaken in these highly productive biotopes.

Forest Resources

Dr M. Oommachan, M.V. Mahavidyalaya, Bhopal pointed out that according to ecological experts, at least one-third of the total area of a country should be covered with forest in order to ensure good climatic conditions, but India falls considerably short of this measure. Therefore, the country is in dire need of an aforestation programme; aside from this, is called for a fresh approach to forestry in order to make it an important sector of economic development. Shri M. Niyamatullah, J.N. Krishi Vishwa Vidyalaya, Jabalpur (JNKVV), pleaded that in order to save forests from human destruction, the concept of social forestry should be promoted through educating the village folk, in particular, as to the importance and maintenance of forests. Prof. S.N. Rao, Marathawada University, brought home the callous role the insect plays in destroying forest wealth by first creating

an imbalance in the ecological conditions and then adjusting itself to it at the cost of the poor plant which it has badly mutilated through defoliation, wood tunneling, sap sucking and root demaging. Prof. D.K. Tiwari of JNKVV, who chaired this session, read a paper on forest resources, which emphasised the ecosystem concept and its dynamics for effective improvement of forest resources and their economic utilization. Prof. Tiwari strongly pleaded that disruption of ecosystem stability would lead to catastrophy and recommended the constitution of ecology teams, long-time research projects of rational development and utilization of forest ecosystems under the leadership of universities, and integrated subject matter extension teams by state departments of agriculture, forestry and agricultural universities, for planning and development of farm and forestry.

Other Resources

Dr H.K. Goswami of Bhopal University reviewed the human genetic diseases. Dr H.S. Sohi, Indian Institute of Horticultural Research, Bangalore, reviewing important diseases of vegetables in India and losses accruing therefrom, pointed out that reliable statistics on losses caused in this country are unfortunately not available and work on these lines is in progress at his institute; and although spraying with chemicals has helped in increasing the yield by 45%, it must be realised that production has to be considerably increased in view of the fact that vegetables constitute an important source of the Indian diet. Dr Y.M. Upadhyaya, I.C.A.R., Indore, discussed utilization of *Triticum* and allied genera in wheat improvement. Dr J.K. Maheshwari, National Botanic Gardens, Lucknow, discussing the biosphere reserve concept in education and research in natural resources, pointed out that, in recent years, much importance has been attached to the concept of biosphere reserves and natural areas system for catering to the needs of basic scientific research, education and training in life sciences. It involves preservation of the entire gamut of life in its totality *in situ* so that it may serve as a natural reference system for the future and provide baselines against which changes in various ecosystems can be evaluated. The following management zones are recognized in biosphere reserves: (i) natural or "core" zone representing *Sanctum sanctorum* of the most natural samples of the biological region and serving as a reference, baseline or scientific study area; (ii) manipulative or "buffer" zone managed for scientific data collection, research, education and training activities, and located to surround the natural or "core" zone; (iii) reclamation or restoration zone managed to study and reclaim lands and natural resources, and serving as a demonstration area for the restoration of other sectors within the biological region; and (iv) stable anthropomorphic or cultural zone serving for research, monitoring, education and training with reference to the study and understanding of traditional cultures and their technologies. Dr Maheshwari made a strong plea that the biosphere reserves are needed in every biogeographical province of the country, viz. Himalayan Highlands, Malabar Rainforest, Bengalian Rainforest, Indus-Ganges Monsoon Forest, Mahanadian, Coromandel, Deccan Thorn Forest, Thar Desert, Laccadives Islands, and Andaman and Nicobar Islands. The universities must reorient life science curricula and establish such reserves, both for research and teaching of the basic concepts of environmental biology. The success of an extensive natural areas system in some American universities indicates that it is fulfilling a vital need for many biologists. Prof. B.K. Behura of Utkal University read the last paper dealing with conservation of crocodiles in India. Dr Behura pointed out that the Indian Crocodilia, represented by three species, viz. the gharial, *Gavialis gangeticus* (Gmelin), the marsh crocodile, *Crocodilus palustris* Lesson, and the salt-water crocodile, *C. porasus* Schneider, are seriously facing extinction in the country. Measures to conserve the reptiles were reviewed, and it appeared that the sanctuaries in Uttar Pradesh and Orissa have made a promising start and are likely to go a long way in augmenting the crocodilian populations for scientific pursuits, recreation and commercial farming.

Summing up the proceedings of the Symposium, Dr B.S. Jangi, Editor, Indian Journal of Experimental Biology, and Indian Journal of Biochemistry & Biophysics, remarked that India's most precious resource, her multitude of people, has unfortunately received but little attention from the standpoint of improving its genetic quality. Centuries of inbreeding, forced by the social evil of caste system, has brought in its wake much misery to our human population through genetic disorders and diseases. Much worse is the continued clinging of our educated, even among scientists, to superstition and obscurantism! No full-blooded and sustained utilization of our magnificient resources is possible under such circumstances. Dr Jangi further suggested that in view of the fact that economic biology is not given place in Indian curricula, Bhopal University should, in the spirit of the symposium, take a lead by including a special paper on this subject in its post-graduate teaching programme under the auspices of the School of Biological Sciences. Dr Ravi Prakash, Vice-Chancellor lost no time in accepting the proposal with both hands and made a spot announcement that economic biology would be one among other disciplines like limnology and biochemistry that would be introduced with effect from the next academic session. Coming back to the subject of utilization of resources, Dr Ravi Prakash struck a right note in being critical of our cultural habits which result in a huge wastage of our food and water resources. Prof. D. K. Belsare, Head of the School of Biological Sciences, Bhopal University and convenor of the symposium proposed the vote of thanks and promised that his School would imbibe the beautiful ideas presented by the learned participants, both formally and informally, during the course of the meet and would leave no stone unturned in promoting the philosophy of meaningful utilization of our natural and human resources.

Chemistry of Tungstates and Molybdates

R. P. RASTOGI, B. L. DUBEY & ISHWAR DAS
Department of Chemistry, Gorakhpur University, Gorakhpur

COMPOUNDS and mixed oxides containing two or more metal ions have been extensively used in a variety of industries as catalysts, solid-state electrolytes, phosphors, refractory materials, non-corrosive pigments, nuclear fuels, fluxing agents and propellants. Aqueous chemistry of tungstates and molybdates up to 1968 has been reviewed by Kepert[1]. Some reviews have also appeared[2-4] on the catalytic activity of molybdates. However, a systematic and comprehensive treatment of the solid-state chemistry of tungstates and molybdates appears to be lacking. In the present communication, the classification, preparation, electrical, magnetic, thermodynamic and other properties as well as applications of these compounds have been reviewed.

Classification of Tungstates and Molybdates

A simple classification of tungstates[5] and molybdates[6] may be given as follows :

Stoichiometric tungstates and molybdates — Most of the tungstates and molybdates belong to this class and may be further classified on the basis of the number of tungsten and molybdenum atoms present. These may be represented by the general formula $M_2X_nO_{3n+1}$ (M, a monovalentatom and X=Mo or W). Thus, tetratungstate has the composition $M_2W_4O_{13}$ and heptamolybdate is represented as $M_2Mo_7O_{22}$. Examples of some tungstates and molybdates of this type are given in Table 1.

Non-stoichiometric tungstates and molybdates — It is well known that many mixed metal oxides show deviations from stoichiometry, resulting in the formation of non-stoichiometric compounds. These non-stoichiometric compounds are of two types: (i) metal or cation deficient (bronzes), and (ii) oxygen or anion deficient. Metal deficient crystals are less common than the oxygen deficient types. Tungsten and molybdenum bronzes, which are non-stoichiometric compounds, are represented by M_xWO_3 and M_xMoO_3, where M is usually one of the alkali metals, and these bronzes are regarded as solid state defect structures in which the holes in WO_3 networks are randomly occupied by alkali metal atoms more or less dissociated into ions and free electrons. Trunov *et al.*[28] found only one tungstate $UO_2.WO_4$ which decomposes in vacuum at 800-900°C to UWO_{5+x}. Compounds with oxygen or anion deficiency are found due to the existence of anion vacancies and interstitial cations.

TABLE 1 — SOME STOICHIOMETRIC TUNGSTATES AND MOLYBDATES

Compound	Formula	Ref.
Alkali metal tungstates	M_2WO_4(M=Li Na, K)	5
Alkaline earth metal tungstates	MWO_4(M=Mg, Ca, Sr, Ba)	5
Aluminium tungstate	$Al_2(WO_4)_3$	5, 7
Indium tungstate	$In_2(WO_4)_3$	7
Thallium tungstates	Tl_2WO_4,$Tl_2W_2O_7$ $Tl_2W_3O_{10}$, $Tl_2W_4O_{13}$ $Tl_{10}W_{12}O_{41}$	5, 8, 9
Tin tungstate	$SnWO_4$	5
Transition metals tungstates	MWO_4(M=Mn,Fe,CO,Ni, Cu,Zn,Cd,Hg),$Sc_2(WO_4)_3$, Ag_2WO_4, $Ag_2W_2O_7$, Hg_2WO_4	5, 7, 10, 11
Rare earth tungstates	$Ln_2(WO_4)_3$(Ln=La,Ce,Pr, Nd, Sm, Eu, Gd, Er, Yb, Lu), $EuWO_4$	5, 7, 12–15
Uranium tungstate	$U(WO_4)_3.XH_2O$	5
Lithium molybdate	Li_2MoO_4	16, 17
Alkaline earth molybdates	M MoO_4(M=Mg,Ca,Sr,Ba)	18, 19
Aluminium molybdate	$Al_2(MoO_4)_3$	7
Indium molybdate	$In_2(MoO_4)_3$	7
Thallium molybdates	Tl_2MoO_4,$Tl_2Mo_3O_{10}$	20, 21
Transition metal molybdates	$MMoO_4$ (M=Mn,Fe,Co,Zn,Cd), $Sc_2(MoO_4)_3$ V_2MoO_8 Ag_2MoO_4	7, 11, 18, 22–25
Rare earth molybdates	$Ln_2(MoO_4)_3$, (Ln=Pr,Nd,Sm, Eu,Gd,Tb,Dy,Lu),Sm_2MoO_7, $EuMoO_4$,Eu_2MoO_7	7, 13, 18, 26

General Methods of Preparation

Tungstates and molybdates have generally been prepared by reactions in the solid state or in solution[5,18] as given below.

Solid-state Reactions

Fusion of metallic oxides and carbonates with MO_3 (M=W, Mo) — Most of the tungstates and molybdates have been prepared by these methods. The general reactions may be written as follows :

$$M_2'O(s) + MO_3(s) \longrightarrow M_2'MO_4(s)$$
$$M_2'CO_3(s) + MO_3(s) \longrightarrow M_2'MO_4(s) + CO_2\ (g)$$
$$M''O(s) + MO_3(s) \longrightarrow M''MO_4(s)$$
$$M''CO_3(s) + MO_3(s) \longrightarrow M''MO_4(s) + CO_2\ (g)$$
$$M_2'''O_3(s) + 3\ MO_3(s) \longrightarrow M_2'''(MO_4)_3(s)$$
$$M_2'''(CO_3)_3(s) + 3\ MO_3(s) \longrightarrow M_2'''(MO_4)_3(s) + 3CO_2\ (g)$$

where M′, M″ and M‴ are mono, bi and trivalent metals respectively.

Phase diagram studies on the system $M_2'O$–MO_3, $M''O$–MO_3 and $M_2'''O_3$–MO_3, etc. have been very useful in predicting the formation of various tungstates and molybdates. Results of phase diagram studies on some tungstates and molybdates are given in Table 2.

Fusion of metal chlorides with sodium chloride and sodium tungstate (or molybdates) — Tungstates of heavier metals, such as Ba, Sr, Ca, Fe, Co, Ni, Mg and Y and molybdates of Zn, Cd, Mn, Fe, Co, Ni and Cu have been formed by the fusion of metal chlorides with NaCl and Na_2WO_4 or Na_2MoO_4. The formation of tungstates and molybdates of s, p, d and f block elements in the solid state is discussed below.

s-Block elements — Gleitzer[16] prepared lithium molybdate by heating MoO_2 with Li_2CO_3 in vacuum at 800-1000°C. Fouassier[36] and Reau[37] also studied the system Li_2O–MoO_2 at 800-1000°C and obtained Li_2MoO_3 and $Li_6Mo_2O_7$. Calcium molybdate was synthesized by Zhukovskii *et al.*[38]. The reaction proceeds in two stages. The first stage, which is a surface reaction, starts in both the cases at 230-250°C. The second stage is an intensive reaction in the bulk, the starting temperature of which is 500°C and 325-350°C respectively depending on the reaction. Barium tungstate is formed when an intimate mixture of BaO and WO_3 in stoichiometric proportions is heated between 300 and 350°C and cooled slowly. The kinetics of the reaction between $SrCO_3$ and MoO_3 in the temperature range 300-700°C has been studied in the solid state. The results obey the Ginstling equation $[1-(1-G)^{2/3}-2/3\ G] = kT$, where G is the degree of transformation; t, the time and k is a constant. Sr_3MoO_6 is formed when $SrMoO_4$ and SrO are brought into contact at elevated temperatures[39]. Its formation shows two kinetically different regions at <900°C with activation energy $E_a = 22\pm 8$ kcal/mole and at >900°C with activation energy $E_a = 103\pm 10$ kcal/mole.

p-Block elements — Aluminium tungstate[40] has been prepared by firing Al_2O_3 with 1-6 moles of WO_3 at 1000°C for 24-48 hr. The only new phase formed is $Al_2O_3.3WO_3$ at 1250°C; the excess Al_2O_3 is found in α-form. Thallous tungstates and molybdates have been prepared in the solid state recently[41]. Thallous tungstates show a series of colours (white, yellow, bluish green and violet) under different conditions of heating and quenching as shown in Fig. 1. Normal bismuth tungstate[5] is formed when an intimate mixture of bismuth oxide and tungsten trioxide in stoichiometric proportions is fused and cooled slowly. It has been observed[21,42] that in solid phase reactions of WO_3 or MoO_3 with some metal oxides (such as PbO, Cu_2O, Bi_2O_3, CdO, MgO, CaO, $BaCO_3$, Co_3O_4), the reagent which has a lower melting point, diffuses over the surface of the second reagent, resulting in the formation of a surface layer. This layer reacts with the substrate material only in the 2-phase contact region.

d-Block elements — Ferrous tungstate has been obtained by the fusion of a mixture of ferrous oxide and tungsten trioxide in the range 480-700°C. $CoWO_4$[10] and $CoMoO_4$[24] have also been formed. Haber *et al.*[24] suggested the mechanism of solid-state reaction of Co_3O_4 with MoO_3. The primary reaction product was found to be *a*-$CoMoO_4$, which was transformed only on cooling and grinding into *b*-$CoMoO_4$ to give products with varying amounts of *a* and *b*. The model of this reaction as suggested by Haber is given in Fig. 2. The solid-phase reaction, $3CuO+WO_3 \rightarrow Cu_3WO_3$ proceeds via the formation of $CuWO_4$ as intermediate[43]. Copper tungstate reacts with CuO in two stages; a surface reaction at 280°C is followed by diffusion into the bulk at 650°C. The activation energy of Cu_3WO_6 formation from $CuWO_4$ and 2CuO is 59 kcal/mole. The formation and properties of $Zn_2W_3O_8$ phase as solid solution with the formula $M(II)Mo_{3-x}W_xO_3$ (M=Mn, Fe, Co, Ni, Zn, Cd) have also been studied[44]. Reaction between Ta_2O_5 and WO_3 was carried out by sintering their mixtures in air or vacuum at 1100-1800°C. In this system, new phases, $3WO_3.Ta_2O_5$ and $3Ta_2O_5.4WO_3$, were found[5].

Table 2 — Phase Diagram Results of Some Tungstates and Molybdates

System	Composition	Ref.
BeO-WO_3	No intermediate formed	29
(MgO,CaO,SrO,BaO)-WO_3	1:1	29
Al_2O_3–WO_3	1:3	29
V_2O_5-MoO_3	1:1	22
Co-W-O	1:1	30
Y_2O_3-WO_3	15:8, 9:4, 3:1, 1:1, 1:3	31
(HfO_2, ZrO_2)–WO_3	1:2	32
La_2O_3-WO_3	3:1, 5:2	33,34
Sm_2O_3-WO_3	1:3, 1:1, 1:2, 3:1	35
Eu_2O_3-MoO_3	1:1, 1:3, 1:4, 1:6, 3:1, 9:4	29

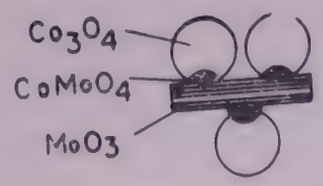

Fig. 1 — Formation of different thallous tungstates under diffrent conditions of heating and quenching

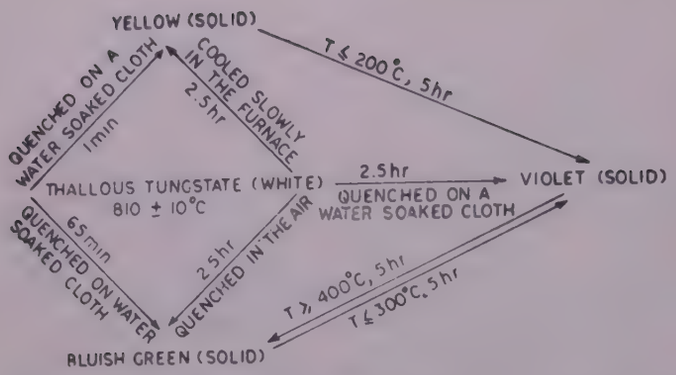

Fig. 2 — Model of the solid state reaction for Co_3O_4-MoO_3 system[24]

The rates of reaction between solid Nb_2O_5 and MoO_3 vapour have been studied gravimetrically at 800-900°C[45]. Transition metal molybdates of the type $MMoO_4$ have been prepared by solid state, precipitation and hydrothermal methods[23]. $HgWO_4$ and $HgMoO_4$ were prepared by firing an intimate mixture of HgO and WO_3 or MoO_3 at 600°C using 50% excess of HgO[46].

Compounds of 4f and 5f elements — In recent years, rare earth tungstates and molybdates have been found to be of considerable interest, both theoretically and technically. Brixner *et al.*[12,26] prepared some $Ln_2[(W,Mo)O_4]_3$ type rare earth tugstates and molybdates. Rare earth tungstates have been prepared by firing stoichiometric mixtures of high purity constituent oxides Ln_2O_3 and WO_3 (Ln=La, Ce, Pr, Nd, Sm, Eu) at 800°C for 10-14 hr and reheating at 1000°C for 4-6 hr. Rare earth molybdates have been obtained by heating the constituent oxides at relatively lower temperatures (600°C) for 14 hr and finally at 700°C for 24 hr. Rhombohedral crystals of $3Ln_2O_3 \cdot MoO_3$ (Ln=Yb, Lu) were obtained by high temperature reactions of Ln_2O_3 and MoO_3[18].

Reactions in solution — Tungstates and molybdates have also been obtained from reactions in solution as described below.

(i) *By crystallization from solution of tungstates, or molybdates in alkali metal hydroxides or carbonates* — Normal tungstates M_2WO_4 (M= alkali metals) and molybdates of alkali metals, Fe, Ni, Co and Cu have been prepared by crystallization from the solution of WO_3 or MoO_3 in metal hydroxides or carbonates.

$$2\,MOH + M'O_3 \longrightarrow M_2M'O_4 + H_2O$$

$$M_2CO_3 + M'O_3 + H_2O \longrightarrow M_2M'O_4 + H_2CO_3$$

where M′=W, Mo

(ii) Some of the tungstates have been prepared from the solution of alkali metal tungstates by metathetical reaction. Thallium tungstates[8,9] and molybdates[20,47] were prepared by the reaction of Tl_2SO_4 with Na_2WO_4 or Na_2MoO_4 in aqueous solution containing different amounts of HNO_3. The reaction is given as

$$Tl_2SO_4\,(aq) + Na_2[W/Mo]O_4 \longrightarrow Tl_2[W/Mo]O_4 + 2Na_2SO_4\,(aq)$$

The principal method of preparing molybdates of Zn, Co and Ni has been double decomposition between an alkali metal molybdate and a soluble metal salt in aqueous solution[48]. Indium molybdate has been obtained by precipitation from aqueous solution of an indium salt and a normal molybdate of a univalent cation[49]. Deluka *et al.*[50] reported the precipitation of barium and strontium molybdates from a solution containing $M(NO_3)_2$ and $(NH_4)_2MoO_4$ at *p*H 10 (M=Ba, Sr). Thallium molybdates of the compositions Tl_2MoO_4, $Tl_2Mo_{2\cdot3}O_{7\cdot3}$ and $Tl_2Mo_3O_{10}$ have also been prepared from reactions in solution[47].

General Properties of Tungstates and Molybdates[18,51]

Simple tungstates and molybdates have the general formulae M_2WO_4 and M_2MoO_4 and contain the discrete tetrahedral ions, WO_4^{2-} and MoO_4^{2-} in crystals. These tetrahedra are regular in alkali metal salts, but may be distorted in salts of other cations. It is now certain that WO_4^{2-} and MoO_4^{2-} are tetrahedral in aqueous solution also. Although both tungstates and molybdates can be reduced in solution, they lack the powerful oxidising property. An electrochemical study[52-54] of solutions of Na_2WO_4 and Na_2MoO_4 in equimolar $NaNO_3$–KNO_3 melt indicates the existence of equilibrium of the following type:

$$2WO_4^{2-} \rightleftharpoons W_2O_7^{2-} + O^{2-}$$

$$2MoO_4^{2-} \rightleftharpoons Mo_2O_7^{2-} + O^{2-}$$

Tungstate and molybdate ions in acid solution polymerize to isopolyions[18] and heteropoly complexes are produced by heating the acidified solutions of tungstate or molybdate with a salt of the central atom in the appropriate oxidation state. On passing H_2S into a tungstate solution, oxythiotungstates and finally the thiotungstate are produced.

$$WO_4^{2-} \rightarrow WO_3S^{2-} \rightarrow WO_2S_2^{2-} \rightarrow WOS_3^{2-} \rightarrow WS_4^{2-}$$

Most of the tungstates and molybdates are insoluble in water. In a solution of sodium tungstate in water labelled with ^{18}O, there is complete exchange between H_2O and WO_4^{2-} in the time required for mixing reagents and separating $BaWO_4$[18]. The properties of some tungstates as discussed by Li and Change[5] are summarized in Table 3.

Optical properties — Certain ions (called activators) when substituted in optical materials (called hosts), can absorb radiation and emit the same as visible or near visible radiation. If the emission occurs within 10^{-8} sec of excitation, the process is called fluorescence. Many of the crystals which fluoresce have been used as lasers. Most of the laser crystals are alkaline earth metal tungstate or molybdate crystals containing rare earth ions. Some tungstates and molybdates doped with rare earth ions have been used extensively in lasers[55]. These are summarized in Table 4.

Magnetic properties — The magnetic properties of 4f compounds have been a subject of considerable interest in recent years[56-59]. The magnetic properties of some rare earth tungstates $Ln_2(WO_4)_3$ (Ln=Nd, Sm, Eu, Gd, Er) have been studied by Dar *et al.*[56] and Lal *et al.*[15]. The magnetic properties of some transition metal tungstates and molybdates were studied by Vanuilert[60]. The type of magnetism, curie temperature θ, and magnetic moment μ in some tungstates and molybdates have been summarized in Table 5.

TABLE 3 — PROPERTIES OF SOME TUNGSTATES

Compound	Properties
Sodium tungstate	White, on heating undergoes two transformations; the transition temperatures between the two polymorphic forms are :

Transition point		Melting point of
$\delta \rightleftharpoons \gamma$	$\gamma \rightleftharpoons \beta$	β—form
570	—	698
564	588	698
564	585	698
572	589	700
587	591	694

Magnesium tungstate	Readily dissolves in hot water
Calcium tungstate	Tetragonal bipyramid
Strontium tungstate	White, translucent, tetragonal bipyramids of density 6·184 g/ml; decomposes on heating
Barium tungstate	Colourless, slightly soluble in water; becomes incandescent at red heat
Tin tungstate	Yellow
Lead tungstate	White, flocculent precipitate, slightly soluble in water; crystals are colourless and octahedral; insoluble in water and nitric acid but soluble in alkalies
Iron tungstate	Light brown powder, trihydrate is insoluble in water, cold HCl, H_2SO_4, HNO_3, dissolves in acids on heating
Cobalt tungstate	$CoWO_4$ — greenish black, $CoWO_4.2H_2O$—violet
Nickel tungstate	Bown, lustrous, translucent rhombic prisms
Copper tungstate	Brown, insoluble in water, soluble in ammonia, phosphoric acid and acetic acid
Silver tungstate	Yellow solid, dark red on melting; with ammonia forms silver tetramino-tungstate (white) which further loses ammonia with the formation of silver tungstate $Ag_2WO_4+4NH_3 \rightarrow Ag_2WO_4.4NH_3 \rightarrow Ag_2WO_4+4NH_3$
Zinc tungstate	Slightly soluble in water
Cadmium tungstate	White
Mercury tungstate	Yellow
Lanthanum tungstate	White; light blue on drying
Praseodymium tungstate	Lavender in colour
Thorium tungstate	White
Ammonium tungstate	White, insoluble in water

TABLE 4 — TUNGSTATES AND MOLYBDATES USED IN LASERS

Host	Doping	Temperature °K
$CaMoO_4$	Nd^{3+}	295
$CaWO_4$	Er^{3+}, Ho^{3+}, Nd^{3+}, Pr^{3+}, Tm^{3+}	77
$PbMoO_4$	Nd^{3+}	295
$SrMoO_4$	Nd^{3+}, Pr^{3+}	295
$SrWO_4$	Nd^{3+}	77

Electrical properties — The electrical conductivities of tungstates and molybdates in the solid state at various temperatures have been measured by several workers[41]. Lal *et al.*[14,60–63] studied the electrical conductivity of $CaWO_4$ (single crystals), $EuWO_4$, $Eu_2(WO_4)_3$ and $Nd_2(WO_4)_3$. Although the electrical conductivity data may be interpreted in terms of (i) band model, (ii) narrow energy band theory, (iii) electron-phonon model, (iv) polaron conduction from band to hopping, and (v) impurity conduction, the data on some rare earth tungstates have been interpreted in terms of conduction due to polarons and various parameters associated with it, such as polaron radius (r_p), coupling constant (α), polaron binding energy (w_p), lattice half band width (J_p). The values of these parameters for some tungstates are listed in Table 6. It has been concluded for $CaWO_4$ that at low temperatures, polaron band conduction is effective, whereas at high temperatures multiphonon assisted hopping mechanism dominates. In the intermediate temperature ranges, the conductivity is the sum of two contributions σ_{opt} and σ_{aco}, the first due to hopping of polarons purely assisted by optical phonons and the second due to the conduction of polarons.

Thermodynamic properties — Some thermodynamic parameters, such as standard heat of formation, standard free energy of formation and standard entropy computed from the experimental results[64] for tungstates and molybdates are listed in Tables 7 and 8.

TABLE 5 — TYPE OF MAGNETISM, CURIE TEMPERATURE AND MAGNETIC MOMENT IN VARIOUS TUNGSTATES AND MOLYBDATES

Compound	Type of magnetism	θ K	μ BM	Ref.
$Nd_2(WO_4)_3$	Antiferromagnetic	–60	3·49	56
$Sm_2(WO_4)_3$	—do—	–30	1·65	56
$Eu_2(WO_4)_3$	—do—	–40	3·39	56
$Er_2(WO_4)_3$	Ferromagnetic	+160	9·50	15
$CoWO_4$	Antiferromagnetic	–85	5·55	60
$NiWO_4$	—do—	–54	3·46	60
$CuWO_4$	—do—	–170	2·23	60
$MnMoO_4$	—do—	–31	5·3	60
$CoMoO_4$	—do—	–9	5·2	60
$NiMoO_4$	Ferromagnetic	+25	3·35	60

TABLE 6 — VARIOUS PARAMETERS ASSOCIATED WITH POLARONS FOR SOME TUNGSTATES

Compound	r_p,Å	α	W_p,eV	J_p,eV	Ref.
$CaWO_4$	1·723	8·013	0·914	1·350	61
$EuWO_4$	1·787	≈10	0·692	10^{-4}	62
$Eu_2(WO_4)_3$	1·992	5·78	0·52	—	63

TABLE 7 — THERMODYNAMIC PARAMETERS OF TUNGSTATES AT 298°K

Compound	ΔH_f° kcal mole^{-1}	ΔG_f° kcal mole^{-1}	ΔS° cal K^{-1} mole^{-1}	Ref.
Li_2WO_4 (c)	—383·2			65
Li_2WO_4 (g)	—240			66
Na_2WO_4 (c)	—369·6	—342·2	38·5	67–69
$Na_2W_2O_7$(c)	—573·8	—528·8	60·8	67,70
$Na_2W_4O_{13}$ (c)	–990·9			67
K_2WO_4 (c)	—377·9			71
K_2WO_4 (g)	—278			72
$MgWO_4$ (c)	—362·7	—336·0	24·18	69,73
$MgWO_4$ (g)	—215			74
$CaWO_4$(c)	—392·2	—366·7	30·27	69
$CaWO_4$(g)	—226			74
$SrWO_4$ (c)	—391	—366	33	75
$SrWO_4$ (g)	—250			74
$BaWO_4$ (g)	—407			76
$SnWO_4$ (g)	—411			74
Sn_2WO_5 (g)	—472			74
$MnWO_4$ (c)	—311·9			77
$FeWO_4$ (c)	—276	—252	31·61	76,78
$CoWO_4$ (g)	—270·7			73
$NiWO_4$ (c)	—269·2			73
$CuWO_4$ (c)	—245·5			73
$ZnWO_4$ (c)	—294·6	—268·5	28·34	78
$CdWO_4$ (c)	—281·8			73
$PbWO_4$ (c)	—271	—247	40·2	79
Ag_2WO_4 (c)	—220·7	—198·9	53	68

g=gaseous state, c=crystalline state

Crystal structure — Tungstates and molybdates crystallize mostly with scheelite or spinel type structures. Tungstates of Ca, Sr, Ba, Pb and molybdates of Ca, Sr, Ba, Pb, Cd have scheelite type structures[55], while tungstates of Li, Na and molybdates of Li, Na, Ag are found to have spinel type structures[55]. The structure type of (Mg, Zn, Cd) WO_4 is wolframite[46], whereas europium tungstate as well molybdate have scheelite type structures[13].

Vibrational spectra of tungstates and molybdates — The physical properties of tungstates and molybdates are intimately related to the structures of these solids. They either belong to the class of compounds which have spinel structure (after the mineral spinel $MgAl_2O_4$

TABLE 8 — THERMODYNAMIC PARAMETERS OF MOLYBDATES AT 298°K

Compound	ΔH_f° kcal mole^{-1}	ΔG_f° kcal mole^{-1}	ΔS° cal K^{-1} mole^{-1}	Ref.
Li_2MoO_4 (c)	—363·3	—37·1	31	65
Li_2MoO_4 (g)	—244			66
Na_2MoO_4 (c)	—350·8	—323·6	38·1	67,79,80
K_2MoO_4 (c)	—358·0	—331·0	45·0	65,81
K_2MoO_4 (g)	—272			71
Rb_2MoO_4 (c)	—357·0	—331·5	56	82
Cs_2MoO_4 (c)	—362·0	+336·3	59·35	83,84
Cs_2MoO_4 (g)	—293			65
$BeMoO_4$ (c)	—330			85
$MgMoO_4$ (c)	—334·8	—309·70	28·4	69,80
$MgMoO_4$ (g)	—224			71
$CaMoO_4$ (c)	—369·5	—344·0	29·3	69,80
$CaMoO_4$ (ppt)	—367·3	—341·8	29·3	86
$CaMoO_4$ (g)	—225			70
$SrMoO_4$ (c)	—369	—343·1	32	65
$SrMoO_4$ (g)	—249			70
$BaMoO_4$ (c, ppt)	—369·4	—344·0	34·5	87
$BaMoO_4$ (g)	—242			88
Ag_2MoO_4 (c)	—200·6	—179·4	54·2	89,65
Tl_2MoO_4 (c)		—226·8		90
$MnMoO_4$ (c)	—284·7			91
$FeMoO_4$ (c)	—257	—233	30·9	92
$PbMoO_4$ (c)			39·7	78

g=gaseous state, c=crystalline state

TABLE 9 — TUNGSTATES WITH HIGH MELTING POINTS[94]

Compound	Melting temperature, °C
$MgWO_4$	1358
$CoWO_4$	1280
$CaWO_4$	1580
3 CaO. WO_3	2250
Al_2O_3. $3WO_3$	1254
$SrWO_4$	1535
$BaWO_4$	1475
3BaO. WO_3	1795

TABLE 10 — TUNGSTATES AND MOLYBDATES AS CATALYSTS IN VARIOUS REACTIONS

Compounds	Reactions	Ref.
(Fe,Ni,Mn,Co,Bi,Al) molybdates	Oxidation of C_3H_6 and NH_3	95
(Bi,Ca,Ni,La)molybdates	Oxidation of CO with $^{18}O_2$	96
$MnMoO_4$	Solid state reduction of Mn_2O_3 and the oxidation of Mn_3O_4	97
$CoMoO_4$ on Al_2O_3	Treating naphthas and gas oils in sour crude oil to reduce mercaptans content	98
$CoMoO_4$ and mixtures of Co and Mo oxides supported on A_2lO_3	Oxidation of H_2S at >4000 ppm	99
Copper molybdate	Oxidation of olefins	100
Sodium molybdate	Production of hydrogen	101
Ammonium molybdates	Production of hydrogen Preparation of calcium silicate	101, 102
α-Bismuth molybdate	Oxidation of propylene IV and 1-butene	4, 103–105
Ferromolybdenum oxide	Oxidation of methanol	106
Ammonium tungstate	Production of calcium silicate	102
V-W oxide (K-63)	Catalysts for oxidative ammonolysis of 2-picoline	107
V_2O_5 -MaO_5 catalyst supported on pumice	Catalytic oxidation of toluene to yield benzaldehyde	108

or scheelite structure (after the mineral scheelite $CaWO_4$). In these structures, the oxygen ions with a radius of 1·32 Å form a cubic close packed arrangement, causing tetrahedral and octahedral interstices. The metal ions are distributed in tetrahedral interstices (surrounded by four O^{2-}) and octahedral interstices (surrounded by six O^{2-}) depending upon their radii. Thus, they may have T_d symmetry or O_h symmetry with respect to oxygen atoms. The IR spectra provide information about the nature of coordination of metal ion with oxygen. For example, tungsten[93] and molybdenum[93] ions in sodium tungstate and molybdate respectively occupy tetrahedral interstices and show an IR absorption band at 835 cm^{-1} and 825 cm^{-1} respectively. It may be expected that the tungsten and molybdenum ions will show T_d symmetry with oxygen in all those tungstates and molybdates which show an absorption band around this frequency.

Applications

Tungstates and molybdates have wide applications as refractory materials, catalysts and pigments.

Tungstates as refractory materials — The alkali metal tungstates have generally very low melting points and are very good fluxing agents. On the other hand, the alkaline earth metal tungstates have high melting points and are used as refractory materials. The melting points of some of the tungstates are given in Table 9.

Tungstates and molybdates as catalysts — Mixed metal oxides are most often oxygen deficient non-stoichiometric compounds, although metal ion deficiency has also been observed in a number of cases. The oxygen deficient compounds possess trapped electrons in the vacant lattice sites, whereas there are some metal ions in higher oxidation state (positive hole) in the latter type. The anionic vacancies with trapped electrons and positive holes act as sites of catalytic activity in a number of chemical reactions. Some of the chemical reactions catalyzed by tungstates and molybdates are given in Table 10.

Molybdates as pigments — Molybdates have been used as pigments[109–114]. Hunn[109] and Kirkpatric *et al.*[114] prepared non-toxic rust inhibiting molybdate zinc oxide pigments. Ziobrowski[110] reviewed molybdate as orange pigments.

Summary

The present review deals with the classification, preparation, properties and applications of tungstates and molybdates. The optical, magnetic, spectral, electrical, thermodynamic properties and crystal structures of these compounds are also reviewed.

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Dye-sensitization in Electrostatic Photography with Special Referencc to Zinc Oxide

J. KUPPUSAMI, A. S. LAKSHMANAN & C. V. SURYANARAYANA
Central Electrochemical Research Institute, Karaikudi 623 006

EXTENSION of spectral response to radiation of longer wavelengths by means of dyes is of interest not in silver halide photography alone; it is equally important in zinc oxide photoconductor electrophotography. Zinc oxide as such is not sensitive to the green or red regions of the spectrum but only to the ultraviolet, its band gap illumination being 3900 Å. To make it responsive to the visible region in the electrostatic copying process, spectral sensitization through the adsorption of a suitable dye is adopted. Spectral sensitization involves increase in the sensitivity of dyed zinc oxide to light of wavelengths longer than that of undyed zinc oxide. The dye confers sensitivity to the portion of the spectrum absorbed by it. Sensitization over a wide wavelength region can be achieved by using a mixture of dyes each sensitizing at different wavelengths.

The dye or dye mix is incorporated by adding it in solution form during the dispersion of zinc oxide in the binder-resin solution prior to its application on the substrate.

The spectral range of various dyes used in electrophotography is shown in Fig. 1, based on the work of Young and Greig[1].

Photosensitivity is markedly affected by the concentration of the dye. Giaimo[2] has studied rose bengal, fluorescein, brilliant green, thioflavin and acridine orange to determine how dye concentration alters photosensitivity.

An undyed zinc oxide layer gives a peak at about 3850 Å in the spectral response curve. When a dye is added at a very low concentration, a second peak, corresponding to the absorption maximum of the dye occurs, while the height of the first peak increases. Increase in dye concentration begins to lower the first peak, while the second peak begins to increase in height. Further increase in dye concentration results in decrease in the heights of both the peaks after a certain stage. The curves obtained by Giaimo[2] using the dye fluorescein are shown in Fig. 2.

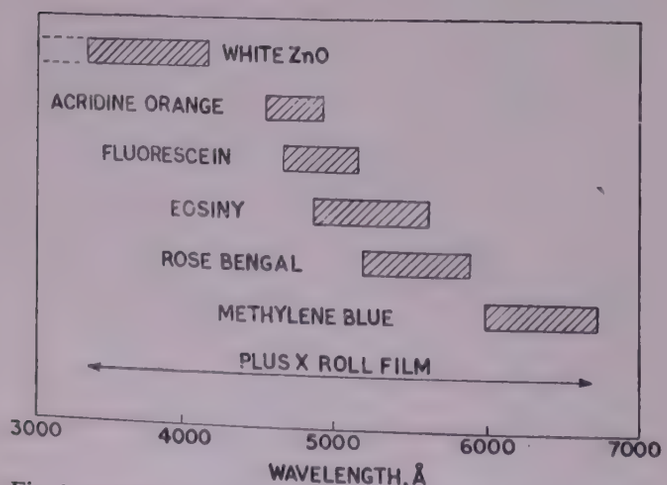


Fig. 1 — Range of spectral response of ZnO layers sensitized with various dyes

The dyes used to sensitize ZnO are strongly adsorbed on the surface of the zinc oxide crystallites. In spite of the continuing research effort on the subject, the theory of dye sensitization is not yet well developed. Energy transfer, charge transfer and p-n junction model have been suggested as possible mechanism to explain dye sensitization. The question as to how the absorption of photons of approximately 1-2 eV in the dye is able to produce free carriers in the semiconductor, though the same effect requires photons of 2·5 eV or more at intrinsic absorption in the semiconductor, has not been answered so far. It has been suggested that the dye molecule, after absorbing a photon of visible light, injects an electron into the conduction band of the ZnO crystallite. This electron then acts as one created by an ultraviolet photon within the crystallite itself.

The vital features of the phenomenon of dye sensitization are: (i) the absorption spectrum of the sensitizer dye adsorbed on ZnO is the same as that of the dye in solution; (ii) the polarity type of the sensitized photocurrent corresponds to that of the sensitized photoconductor; and (iii) photovoltaic effect is exhibited by the dye-layer-photoconductor junction.

In addition, in the case of electrofax layers, the dye is supposed to be chemisorbed and the photocurrent is proportional to the square root of light intensity.

In ZnO, chemisorbed oxygen plays an important role in photoconduction. Electron affinitive molecules, such as phthalic anhydride have been studied keeping this in view. Preliminary results appear

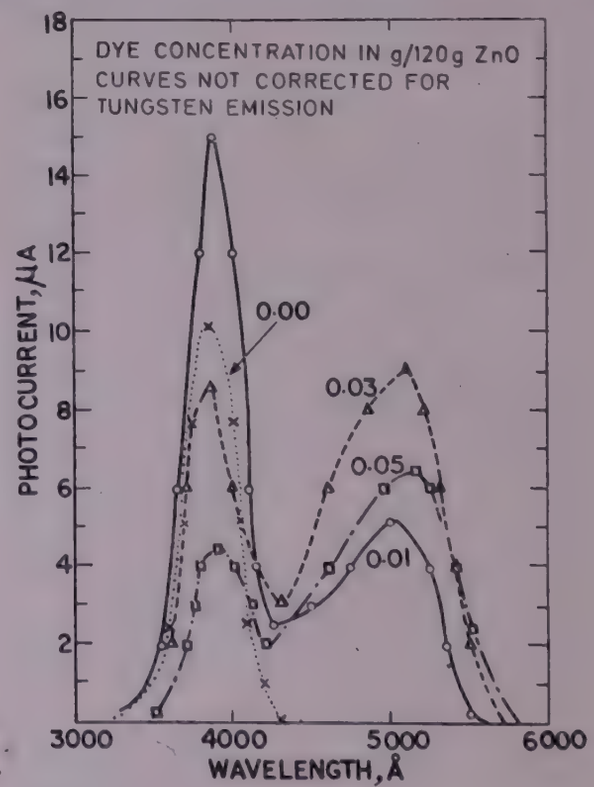


Fig. 2 — Effect of dye concentration on spectral sensitivity of ZnO layers (dye, fluorescein)

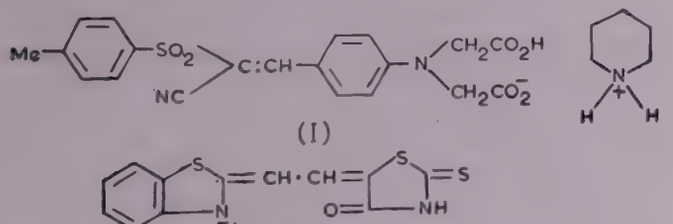
to suggest that the surface states are modified by chemical sensitizers and make photoelectrons longer-lived. The existence of adsorbed oxygen was found to be essential for chemical sensitization by electron affinitive molecules. It has also been observed that the efficiency of spectral sensitization of ZnO increases when dyes are adsorbed on it together with materials like phthalic anhydride or other electron affinitive molecules. This is generally referred to as 'hypersensitization'. In dye-sensitized excitation of zinc oxide surfaces also, photodesorption of oxygen occurs in parallel with photoconduction. From experimental results, it has been proposed that at 25°C, most of the oxygen is chemisorbed as O^-_2, at 140°C as O, and at 280°C or higher temperatures as O^{2-}.

A study[3] was made on the sensitization effect of molecular complexes of poly (N-vinyl carbazole) with chloranil, bromamide and tetracyanoethylene on polycrystalline ZnO. It was found that the adsorption of the component with charge transfer also induced chemical sensitization.

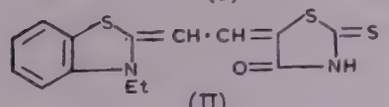
Absorption measurements[4] on ZnO crystals treated with merocyanine dyes indicated that the quantum yield is limited by electron trapping.

Spiropyrans with substituted carbonyl groups were adsorbed on ZnO to study the efficiency of optical sensitization[5]. One type of dye was found to be attached to ZnO strongly by chelating with the lattice zinc and this type exhibited a high efficiency. A lower efficiency was shown by the type that chelates weakly.

The effect on single crystals of ZnO of the following dye types has been studied.



(I)



(II)

The dyes were vapour deposited on to the crystals in ultrahigh vacuum to avoid any possible solvent effect and to exclude any adsorbed gases. These dyes have been found to increase the density of surface states near the Fermi level[6].

Thin ZnO films sensitized by spraying rhodamine B have been observed to show an unusual self-quenching, which is explained as being due to the injection of photoelectrons from the dye to ZnO and recombination of holes with the electrons trapped by oxygen adsorbed at the ZnO surfaces[7].

The adsorption of uranine and rhodamine B on pure ZnO of varying non-stoichiometry, obtained by doping with monovalent and trivalent cations has been studied[8]. It has been found that uranine in aqueous solutions is chemisorbed to the extent of 10% and adsorbed with lower energy to the extent of 90% on undoped ZnO; the total adsorption increases when ZnO is made strongly n-type. On the other hand, Li doping reduces both types of adsorption markedly. When alcoholic solutions of uranine were used, only chemisorption was found to be affected by non-stoichiometry.

Rhodamine B, which is a basic dye, chemisorbs exclusively on doped and undoped ZnO surfaces, from both aqueous and alcoholic solutions, Li doping increasing and Al doping decreasing the chemisorption.

The quantity of chemisorbed uranine on highly pure polycrystalline zinc oxide in natural light has been found to be about 60% greater than that in the dark. In ultraviolet light, the chemisorption increases three-fold, with decrease in physisorption and the total adsorption. In the case of rhodamine B, exclusive chemisorption increases in room light and is nearly doubled in ultraviolet light[9].

Adsorbed erythrosin was found to chemically desensitize the semiconducting properties and to sensitize photoconduction in ZnO[10]. Increase in dye concentration lowered dark decay slightly up to a certain concentration ($0{\cdot}3 \times 10^{-6}$ moles of dye/mole of ZnO) beyond which it decreased rapidly. This has been explained as being due to increase in the depth of electron capture levels at low concentrations. At high concentrations, the dye induces electron depletion in the lower region of energy with a transition to the higher energy band.

The chemical desensitizing effect of erythrosin can be corrected by the adsorption of a chemical sensitizer like maleic anhydride on dye-sensitized ZnO[11]. The adsorbed chemical sensitizer and the spectral sensitizer together cause changes in the local energy states.

In the case of merocyanine dyes a strong electronic interaction between the dye molecules and ZnO has been observed even in the dark[12]. The n-type conductivity of ZnO is affected. If ZnO is pretreated with gases prior to dye absorption, the dark surface conductivity varies by several orders of magnitude. It has been found that the sensitized photoconductivity is positive for a low dark surface conductivity and negative for a high dark surface conductivity.

The rate of dark decay of panchromatically sensitized ZnO binder layers increases as the degree of spectral sensitization increases. Also, light decay increases rapidly to a maximum and thereafter decreases gradually[13].

The adsorption of dyes has been found to induce a change in the dark conductivity and the magnitude of the change represents the sensitizing power of the dye[14]. Photoinjection of electrons is assumed to occur from surface states to the bulk and depends on the population of the surface states. The effect of temperature is accounted for by assuming a critical surface level, the surface states located below which are assumed to make no contribution to the sensitization.

Based on the electronic structures of the photoconductors and dyes, the reflection spectra in the visible range and the adsorption state of the dye, it has been suggested that the electronic structures of the dyes are not influenced markedly by their adsorption and the sensitization takes place due to the injection of electronic charge carriers from the excited dye molecule into the photoconductor[15].

It is proposed that in the dark, there is a build-up of an electrostatic field between the dye and the

inorganic systems (CdS, ZnO, etc.) as a result of transfer of electrons or holes from the semiconductor or vice versa and the sensitization is due to the separation of optically formed electron-hole pairs by the internal field[16]. A mathematical treatment for the transfer mechanism and the calculation of the quantum yield of charge carriers in the dye is given by Nelson[17].

Studies on the voltage-amperometric characteristics of electrophotographic layers deposited on Teflon indicated that charge carriers were transferred by a Schottky mechanism, as evidenced by an approximate linear increase in the current with increasing voltage, when plotted in Schottky co-ordinates and also by a linear increase in conductivity with temperature[18]. The adsorption of small amounts of erythrosin on ZnO did not change the transfer mechanism. But this reduced the current at a given voltage, while large quantities (10 mg/g of ZnO) change the mechanism from Schottky transfer to tunnelling.

A study of ZnO electrodes, highly and moderately doped, in rhodamine B solutions with and without hydroquinone, shows that the excited energy levels of the sensitizer lie at the same energy as the conduction band of the ZnO electrode[19]. Electron injection from the excited dye leads to the formation of oxidation products which can be regenerated; this is indicated at highly doped electrodes by a reduction current. This cathodic current consists of tunnelling conduction electrons and thereby substantiates the electron transfer mechanism. At highly doped ZnO electrodes, a fraction of the excited dye molecules becomes deactivated by energy transfer to conduction electrons (intra-band excitation) leading to quenching and reduction of the sensitization current.

The current problems of dye sensitization of ZnO have been discussed by Inoue[20]. A new model taking into account the variance in population of the surface electrons on ZnO resulting from interaction between ZnO and the dye has been postulated. This involves a critical surface level below which the surface states do not contribute to the sensitization. Temperature dependence of the sensitization efficiency is explained by the change in the density of the surface electrons above the critical level with temperature.

EPR studies[21] and the electrochemical cell technique[22] have been employed as tools for investigating the mechanism of sensitization. In particular, the electrochemical cell technique is used fors tudying the electron transfer mechanism. A mixture of rhodamine B and 1,2-(hydroxyphenylazo)-2-naphthol gave optimum sensitization in a basic electrolyte, indicating mutual interchange of dyes sorbed on ZnO. The application of the above technique is justified from experiments with ZnO-resin layers doped with the same dye mix in the cell.

To measure the extent of sensitization, it was necessary to determine the quantity of dye adsorbed on the ZnO surface. The extent of dye adsorption on the surface can be inferred from the adsorption isotherms in aqueous electrolytes for rhodamine B and eosin.

The electrochemical cell technique is illustrated in Fig. 3. The ZnO single crystal in a sample holder

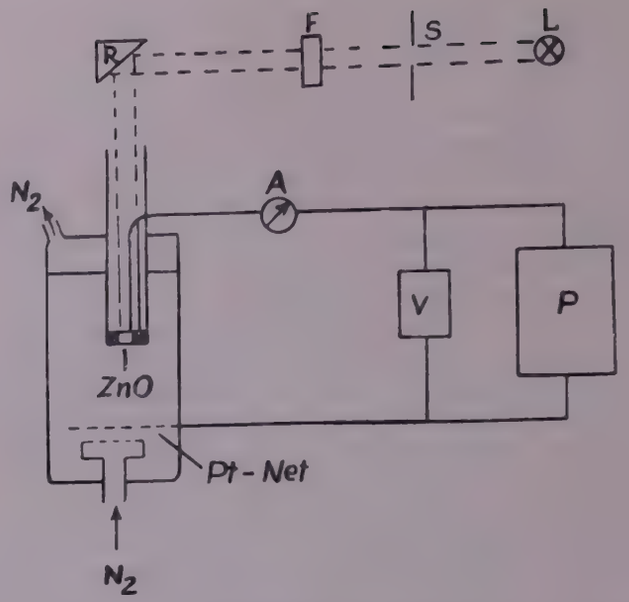


Fig. 3 — Set-up for electrochemical cell technique [P, potentiostat; V, electrometer; A, picoammeter; R, reflecting mirror or prism; F, interference filter; S, shutter; and L, light source]

is kept in contact with the electrolyte. A transparent indium film on the backside of the crystal is used as the electrode. As shown in Fig. 3, the illumination is effected from the backside to avoid absorption while light passes through the electrolyte solution coloured by the dye. The set-up can be maintained at constant temperature with facility to pass gases through the system. A xenon lamp is used as the light source. A sensitive ammeter for current measurement and electrometer for voltage measurement are used. A potentiostat maintains a constant voltage. Measurements are made in an electrolyte containing KCl buffered with sodium acetate-acetic acid solution to a *p*H of 4·5. For rhodamine B and methylene blue, 0·1*N* acetate buffer + 0·5*N* KCl and for eosin 0·05*N* acetate buffer + 0·25 *N* KCl are used.

In the dark, the current with an anodically polarized ZnO electrode is very small both in the absence and presence of sensitizers and is almost independent of the applied voltage. Under illumination with the same photon flux at $\lambda = 545$ mμ (for rhodamine B) and 502 mμ (for eosin), and with the same quantity of adsorbed dye, the current density rises for a rhodamine B sensitized crystal from 10^{-9} A/cm^2 to $1{\cdot}3 \times 10^{-7}$ A/cm^2 and for an eosin sensitized crystal from $1{\cdot}3 \times 10^{-9}$ A/cm^2 to $2{\cdot}5 \times 10^{-7}$ A/cm^2. The anodic photocurrent is proportional to light intensity in the presence of rhodamine B and eosin. This suggests that charge carriers are passing from the dye into ZnO and their current is proportional to the light intensity.

To get more information on the mechanism, discharge measurements were made on charged layers. The decay of the surface potential under illumination with light of different wavelengths was studied. It was found that at a dye concentration greater than about 10^{-6} mole/m^2 of ZnO, eosin is a better sensitizer. This is in agreement with the results of anodic current measurements. At these high concentrations, it is supposed that rhodamine B precipitates as small

crystals around ZnO grains, resulting in poor photoconductivity in the presence of oxygen. This explains the decrease in the sensitizing ability of rhodamine B with increase in concentration. But the sensitizing ability of eosin increases with increase in concentration and tends to a constant value. The sensitizing action of rhodamine B on the anodic photocurrent falls significantly with the simultaneous presence of methylene blue in the electrolyte.

Estimations of work function of polycrystalline ZnO covered with organic dyes have been made by measuring the potential difference between the ZnO powder layer (with and without dye) and a gold reference electrode using the Kelvin method[23]. The work function (ϕ) of zinc oxide covered with rose bengal increases with increase in adsorbed dye concentration, reaches a maximum at 5×10^{-7} mole of dye/g of ZnO and then decreases as the concentration of the dye increases further. ϕ_{ZnO} is constant at concentrations $< 76{\cdot}5 \times 10^{-7}$ mole/g of ϕ_{ZnO}. In air, for undyed polycrystalline ZnO, ϕ_{ZnO} is 4·7 eV and the maximum value for dyed ZnO is 4·82 eV. The adsorbed dye effects only a small change in the work function of ZnO. A model has been proposed by Kikuchi *et al.*[23] based on the analysis of the dipole moment of the adsorbed dye and the potential barrier height formed by the coverage of dye on ZnO grains.

In general, organic dyes are found to be extremely good spectral sensitizers in view of the minimum geometrical changes and maximum redistribution of charges on absorbing light[24]. Dyes whose dark Fermi energy levels lie below the electron affinity of ZnO are good sensitizers for ZnO and those lying above are poor sensitizers.

Adsorption of 3,3′-diethyl-9-methyl thiacarbocyanine bromide, 1,1′-diethyl-2,2′-cyanine iodide, methylene blue, phenosaframine, rose/bengal, erythrosin and eosin from aqueous solutions by both TiO_2 and ZnO was studied[25]. All these dyes were adsorbed by TiO_2, some following the Langmuir isotherm. But on ZnO only the acid dyes showed significant adsorption and these dyes are good sensitizers for ZnO.

Inorganic salts were also used to sensitize ZnO[26]. The anodic photocurrent through single crystals of ZnO sensitized with rhodamine B increased in the presence of halide ions (especially I-ions) according to a co-sensitization mechanism.

Summary

Unsensitized zinc oxide-resin coatings have peak sensitivity in the near ultraviolet region (370-390 mμ) corresponding to the intrinsic band gap energy of 3·2 eV for ZnO, with some sensitivity extending into the violet end of the visible spectrum. This sensitivity can be increased enormously through the addition of selected organic dyes, which are strongly adsorbed on the ZnO crystallites, the increase in sensitivity being the result of the extended spectral response of the layer. This article gives an account of the vital features of dye-sensitization, the various dyes employed for the purpose and some of the possible mechanisms of sensitization.

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Predictive Approaches for Cation-Exchange Equilibria in Soils

R. PAL & S. R. POONIA
Department of Soils, Haryana Agricultural University, Hissar

In easily accessible surfaces like that of kaolinite in contrast to montmorillonite (where most of the exchange occurs between the aluminosilicate sheets), the rate of exchange is very rapid. Expressions correlating equilibrium compositions of the exchange complex and the solution are important because they enable the prediction of changes in the adsorbed and solution phases in soil as influenced by fertilizer application, addition of irrigation and waste waters, ion uptake by plants, etc. Soil scientists have been striving since long for an exchange equation capable of enabling accurate predictions to be made. Many exchange equations and theories based on different assumptions have been propounded[1–9].

Three approaches are normally adopted in deriving equations to represent the distribution of ions between an exchanger and its equilibrium solution. The first is the purely formal thermodynamic treatment introduced by Argersinger *et al.*[10] and developed further by Gaines and Thomas[9]. The second approach involves microscopic description of the process of exchange through the standard diffuse double layer theory introduced by Gouy[11], applied to soil systems especially for negative adsorption by Schofield[12], to cation-exchange equilibria by Eriksson[7] and simplified by Bolt[8]. The third is the empirical approach, wherein the most widely used equation is that of Gapon[4], which represents a simple relationship between soluble and exchangeable mono- and divalent cations in soils or clays at equilibrium. This type of equation has been successfully applied in the case of soils of arid and semi-arid regions[13].

Babcock[14] has described a theory concerning the chemical properties of soil colloidal system at equilibrium. Bolt[15] has reviewed the cation exchange equations as they are being used in soil science. In the present article, an attempt has been made to review critically the predictive approaches used by various workers. It has also been attempted to examine/explain experimental results on cation exchange equilibria in different soils and clays. The methodologies used by different workers for cation exchange equilibrium studies are also reviewed.

Methodology for Cation Exchange Equilibria Studies

Preparation of homoionic soil — To conduct cation exchange equilibrium studies, generally the use of homoionic soils/clays is preferred for reasons of experimental convenience and accuracy in the estimation of the cation pair involved. A homoionic soil is prepared by repeated washings of the soil with chloride salt solution ($\approx$ 1 *N*) of the concerned cation, using centrifugation or leaching technique. While doing so, it should be ensured that all the exchange sites are freely accessible (i.e. the soil is thoroughly dispersed) to the equilibrating cation. The homoionic form of the soil can be ensured by (i) ascertaining the absence of other cations or (ii) measuring the changes in the concentration of the equilibrating cation in the equilibrating solution/leachate. In this case, approach (i) is preferred over approach (ii), since the negligible changes in the concentration of the equilibrating cation are difficult to measure accurately. Five successive washings with soil and solution in the proportion 1:5 (by wt) for the centrifugation procedure or leaching a limited amount of soil ($<$ 500 g) with 25 times its weight of the solution usually leads to a nearly homoionic soil. The soil can be made nearly salt-free by two successive washings with distilled water, four washings with 95% ethanol and two washings with petroleum ether (soil-liquid ratio 1:5). Excessive washing with water, however, may cause hydrolysis of the adsorbed cations, particularly of those having a large water hull around them. Although theoretically it is impossible to prepare a true homoionic soil because of interference due to continuous dissolution of soil minerals, the error caused is negligible from practical considerations. However, its omission will be unwarranted in preparing monoionic system from calcareous soils.

Equilibration procedure — The homoionic soil is equilibrated with a solution of the replacing cation(s) using (i) different volumes of a solution of the same concentration; (ii) same volume of a solution of different concentrations; (iii) repeated washings with solutions of different compositions; or (iv) the dialysis technique. The time taken for equilibration is a few hours, provided the soil is fully dispersed and the cations are of non-fixing type. As a matter of fact, in such a situation, the major part of exchange ($>$ 95%) takes place within a few minutes; a longer time is allowed to ensure complete equilibration, particularly for heavy soils.

Estimation of equilibrium exchangeable cations — Generally, the estimation of cations on the exchange complex is carried out in two ways. (i) Stripping technique: In this procedure, two approaches are adopted: (a) The soil in equilibrium with the solution is washed free of soluble salts with alcohol and then it is extracted in a salt solution ($\approx$ 1*N*) (free from the cations on the exchanger); or (b) the soil with the equilibrium solution is centrifuged, the supernatant liquid collected for analysis and the equilibrium solution left in the soil under study measured. The total cations extracted in the salt solution minus the cations in the equilibrium solution left designate the exchangeable cations. From reliability point of view, procedure (b) has a slight edge over procedure (a). However, at low electrolyte concentrations, particularly with a larger fraction of the monovalent cation ($>$ 90%), the error involved in procedure(b) is significant because of negative adsorption. (ii) Isotopic dilution technique: A given amount of soil (1 g) with a known volume of untagged equilibrium solution (5 ml) is mixed with an equal volume of tagged solution of the same composition. The contents are fully dispersed and equilibrated for 48 hr on a shaker. The equilibrated soil suspension is centrifuged and the radioactivity is

measured in the supernatant liquid using a suitable radiation measuring device. The amount of adsorbed cation (A_x) is calculated from:

$$A_x = [(\text{CPM control}/\text{CPM test})-1]\ \text{Total } A \text{ solution}$$

The Thermodynamic Approach

Assuming the system to consist of two distinct phases, i.e. an exchange phase and a solution phase, the law of mass action can be applied. The process of cation-exchange may be represented as the interchange of ions between the exchange phase and the solution phase as follows :

$$n_{Ae}\ Ae + n_B\ B \rightleftharpoons n_A\ A + n_{Be}\ Be \qquad ...(1)$$

where n with subscripts A and B represents the number of reacting ions A and B, respectively; the subscript e denotes ions in the exchange phase, while the absence of e denotes ions in solution.

From classical thermodynamics, one has :

$$G = \bar{G}_i\, n_i$$

where n and $\bar{G}$ denote the number of moles and partial molar free energy, i.e. chemical potential (μ), respectively. Introducing the definition of the ion activity a as

$$\mu_i = \mu_i^\circ + RT \ln a_i$$

and Gibbs free energy change during the reaction as

$$\triangle G = \Sigma\ \mu_i n_i \text{ (prod.)} - \Sigma\ \mu_i n_i \text{ (react.)}$$

one gets

$$\triangle G^\circ_r = -RT \ln K \qquad ...(2)$$

where $K = a_A^{nA}\ a_{Be}^{nBe} / a_{Ae}^{nAe}\ a_B^{nB}$ is the thermodynamic equilibrium constant; R, the universal gas constant; and T, the absolute temperature. The superscript o denotes the standard state.

The Standard State

In Eq. (2), the standard Gibbs free energy of exchange is defined in terms of the equilibrium values of the activities of reactants and products. Its value depends upon the standard state chosen for the different components. Hence, Eq. (2) cannot be applied without further specifications. Babcock *et al.*[16] suggested the same standard state for both the ions on the exchange and in solution. This evidently amounts to $\triangle G^\circ$, and $K=1$. Since this choice of the standard state makes all the thermodynamic equilibrium constants equal to unity, it is less informative regarding the distribution of the cations.

For the interpretation of the experimental data on equilibrium between cations in solution and on clays, Gaines and Thomas[9] suggested that soils in homoionic state in equilibrium with infinitely dilute solutions of the salt of that cation are in their standard state. Babcock[14], however, pointed out that because of the hydrolysis of weakly adsorbed cations at vanishing concentration, the adsorbed ions would no longer remain at unit mole fraction. According to Bolt[15], by the arbitrary choice of the standard state of the exchanger, as suggested by Gaines and Thomas, it becomes a measure of the relative affinity between the exchanger and the cations concerned, and this enables one to compare different cation pairs (and the same exchanger) or different exchangers (and the same cation pair).

To obtain a cation exchange equation, a theory must be found for the activity of ions in the exchanger phase. Vanselow[3] assumed that the exchanger phase could be treated in analogy with an ideal solid solution, according to which the activities of the adsorbed ions are set equal to their mole fractions M in the exchanger phase. Argersinger *et al.*[10] extended Vanselow's theory to non-ideal exchangers and introduced activity coefficient f for the adsorbed ions, defined as $f_i = a_{ie}/M_{ie}$

Substituting Eq. (2) into Eq. (1), we get:

$$K = \frac{f_B^{nBe}\ M_{Be}^{nBe}\ a_A^{nA}}{f_A^{nAe}\ M_{Ae}^{nAe}\ a_B^{nB}} = \frac{f_B^{nBe}}{f_A^{nAe}} K_c \qquad ...(3)$$

where K_c is the selectivity coefficient. To influence the activity coefficients of adsorbed cations, in addition to the long range electrostatic forces, other short range forces are also operative[17]. Simplifying the treatments of Argersinger *et al.*[10] and Gaines and Thomas[9] for calculating the activity coefficients of the adsorbed ions and the thermodynamic exchange constant, Deist and Talibudeen[18,19] used the following expressions for a monovalent-divalent cation exchange reaction :

$$\ln f_+^2 = (1-x)\ (1 - \ln\ K_c) + \int_x^1 \ln\ K_c\ dx \qquad ...(4)$$

$$\ln\ f_{++} = -(x)\ (1-\ln\ K_c) - \int_0^x \ln\ K_c\ dx \qquad ...(5)$$

$$\ln K = -1 + \int_0^1 \ln K_c\ dx \text{ (for monovalent-divalent exchange)} \qquad ...(6)$$

$$\text{or}\quad \ln K = \int_0^1 \ln K_c\ dx \text{ (for mono-mono or di-divalent exchange)} \qquad ...(7)$$

where x is the equivalent fraction of exchange sites occupied by monovalent cation.

Besides being only approximate (because of the neglect of the change of solvent activity during the exchange), Eqs. (6) and (7) require a knowledge of the ratio of activity coefficients in a mixed electrolyte solution to calculate K from the experimental values of K_c obtained at a finite total concentration of the equilibrium solution. However, both the difficulties disappear if the value of K_c is obtained from the linear extrapolation of plots between log K_c and the square root of twice the ionic strengths at different concentrations of the equilibrium solution, to zero ionic strength[20,21].

This procedure allows calculation of the values of thermodynamic exchange constant K corresponding to a particular choice of the standard state for the surface phase, viz. that of the homoionic exchanger in equilibrium with an infinitely dilute solution of the corresponding salt.

The activity coefficient, γ_i of the ions in solutions having ionic strength $<0{\cdot}3$ mole/litre can be calculated using the well known Debye-Huckle equation,

$\log \gamma_i = -AZ_i^2\sqrt{I}/1 + aB\sqrt{I}$. The equation given by Davis, viz. $\log \gamma_i = -AZ_i^2[(\sqrt{I}/1+\sqrt{I} - 0{\cdot}2\,I]$, can be used for solutions having ionic strength up to 0·5 mole/litre with reasonable accuracy. In these equations, A and B are constants, their values depending on temperature and dielectric constant; a is the radius of the hydrated ion; and $I = 0{\cdot}5\,\Sigma_i\, C_i\, Z_i^2$ with C (mole/litre) as the concentration; and Z, the valence, is the ionic strength.

The thermodynamic approach of Argersinger *et al.*[10] with regard to exchange equilibria, extended by Gaines and Thomas[9], has been tried on clays and soil systems by several workers[18-20,22-27]. These workers tried to calculate the standard free energy changes

$$\Delta G^\circ = -RT \ln K$$

enthalpy changes

$$\Delta H^\circ = -4{\cdot}576/(1/T_2 - 1/T_1) \log (KT_2/KT_1) \quad ...(8)$$

and entropy changes

$$\Delta S^\circ = (\Delta H^\circ/T) - (\Delta G^\circ/T) \quad ...(9)$$

of cation exchange reactions in clays and soil systems. In these equations, T_1 and T_2 are the absolute temperatures at which the change was studied. The sign and magnitude of the above quantities determine whether a certain cation is preferred by the exchanger over another one (Figs. 1 and 2).

Recently, Ravina and De Bock[28] suggested an alternative procedure based on the theory of irreversible thermodynamics for the calculation of standard free energy change (ΔG°) in the case of mono-monovalent exchange. According to them, the thermodynamic

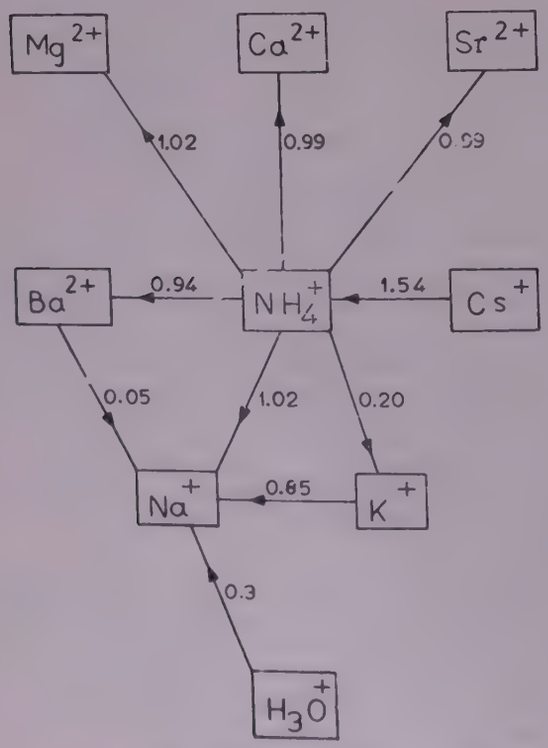

Fig. 1 — Standard free energies of exchange (kcal eq^{-1}) in a montmorillonite clay[27]

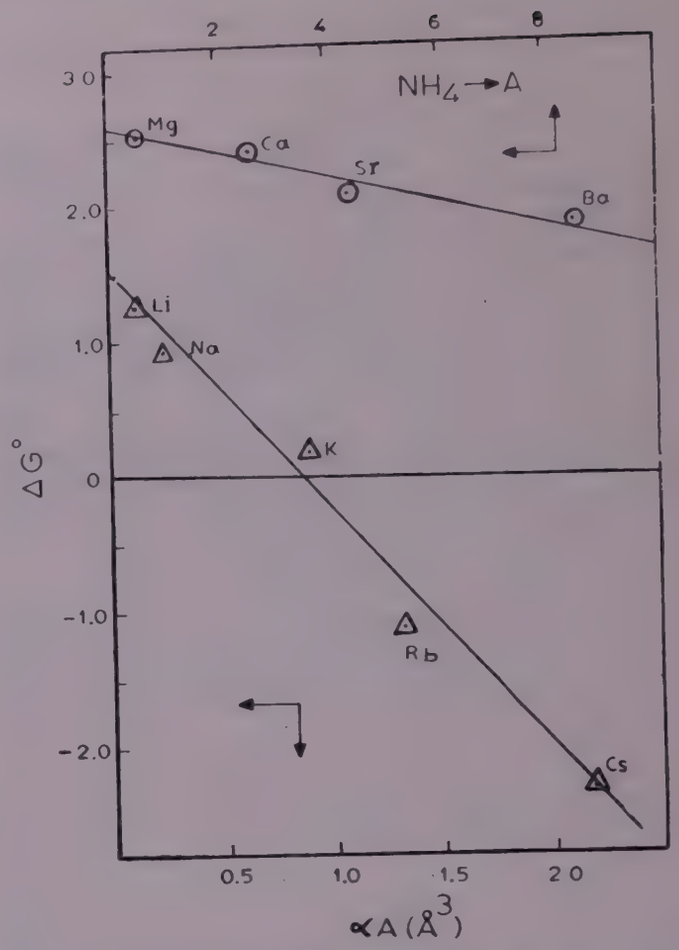

Fig. 2 — Relationship between standard free energy of exchange (ΔG°, kcal eq^{-1}) and polariziability (A) of cation substituting NH_4 in a montmorillonite clay[27]

exchange constant K may be calcuated as :

$$K = \frac{C_2\, C_{1_0}}{C_1\, C_{2_0}} = 1/\exp\left\{\frac{1}{RT}\left[\left(P_R - \frac{\beta P_R}{2}\right)\left(V_{1_0} - V_{2_0}\right)\right]\right.$$

$$\left. + \frac{\varepsilon+2}{3} N \frac{E^2}{2} (a_1 - a_2) - NF\, ae\, (Z_1 \phi_1 - Z_2 \phi_2)\right\} \quad ...(10)$$

where C, V and a denote the concentration of ions near the surface of the clay particle, intrinsic volume of ions in bulk solution and polarizability of ions in the diffuse double layer, respectively; subscripts 1 and 2 stand for the two monovalent ions near the surface of the clay particles and $1_\circ$ and $2_\circ$ for the equilibrium solution; P_R is the pressure in the diffuse double layer ($1{\cdot}17 \times 10^9$ dyne cm^{-2}); β, the compressibility ($32{\cdot}83 \times 10^{-12}$ cm^2 dyne^{-1}); ε, the dielectric constant ($\approx$29); E, the macroscopic electrical intensity; N, e, z and ϕ stand for Avogadro number, electronic charge, valency and electrostatic potential, respectively; and RT is equal to 0·596 kcal mole^{-1}. In Eq. (10), F seems to be superfluous; this can be ascertained from the principle of homogeneity of dimensions. Based on this non-empirical approach, the calculated values of ΔG° were found to be in agreement with the experimental values of Martin and Laudelout[29].

Whether a particular cation is preferentially adsorbed to another in an exchange reaction can also be seen from the shape of the normalized exchange isotherm (equivalent fraction of the cation on the exchange

versus equivalent fraction in solution). The cation is preferentially or non-preferentially adsorbed, if the shape of its normalized exchange isotherm is convex or concave upwards, i.e. the exchange isotherm lies above the diagonal or below it. In so far as exchanges between cations of similar valence are concerned, the above criterion for selectivity works. But in the case of exchanges between cations of different valencies, one should see the position of the exchange isotherm with respect to the position of the non-preference isotherm based on the valence effect. Jensen and Babcock[25] expressed a similar opinion about preferential or non-preferential adsorption of a cation in a mono-divalent exchange. From their study of K-Mg and K-Ca exchange in Yolo loam, they reported that although the normalized exchange isotherms for K were concave upwards below the diagonal, they did lie over the non-preference exchange isotherm based on the valence effect.

The preference for an ion by the exchanger on the basis of the shape or position of its exchange isotherms or the sign of the standard free energy changes does not necessarily mean that the cation is more strongly bound. This is because the free energy is determined by the enthalpy and entropy, and the binding strengths are normally defined in terms of enthalpy alone. The smaller the enthaply content, the stronger is the binding. The extent of the C-spacing of most 2:1 type of minerals, which depends upon the saturation of a cation, is also attributed to the less binding of a divalent compared to that of a monovalent cation. Deist and Talibudeen[18,19] found that most 2:1 type clay minerals have a larger C-spacing, when they are Ca rather than K saturated. If, then, the Ca ions are held midway between adjacent silicate sheets (as suggested for Mg in vermiculite by Mathieson and Walker[30]), the Ca ion will be farther away from the surface than the K ion. This tends to diminish the effect of the divalent ion on the binding energy.

It is evident from Eq. (3) that the thermodynamic exchange constant K can be determined provided the values of K_c, f_+ and f_{++} can be calculated using Eqs. (3), (4) and (5) respectively. Laudelout *et al.*[20], however, suggested that if the values of log K_c obtained at different electrolyte levels are plotted against the square root of the ionic strength and then linearly extrapolated to zero ionic strength, the values of the thermodynamic exchange constant so calculated for log K_c at zero ionic strength represent the choice of standard state and hence are independent of solution concentration.

The relative freedom of movement of adsorbed ions at different degrees of saturation of the various ions can be interpreted on the basis of the values of their activity coefficients.

Activity Coefficients of the Adsorbed Ions

For a normal cation exchanger, the activity coefficient, f_i of any adsorbed ion i should increase with saturation of the exchange complex with cation i, ultimately approaching the theoretical, $f_i = 1$. In case f_i decreases with i saturation, i.e. increase in saturation of the complex with i increases its binding strength, the results seem to be anomalous. Deist and Talibudeen[19] found f_{Ca} to decrease with K saturation, and f_K to increase first and then decrease with K saturation of the exchange complex in a K-Ca soil system. They explained this anomalous behaviour on the basis of the distribution of the ions in the Stern-Gouy layers of the diffuse double layer and the change in the inter-layer spacing of the 2:1 clay minerals on saturation with various ions. Heald *et al.*[31] admitted a preference factor for the Stern layer, whereas the remainder Gouy layer of the double layer was assumed to be sensitive only to the valence of the ion. The preference constant for the Stern layer was then introduced as a formation constant for an ion-surface carrying reaction. They limited their attempts to working out the equation, assuming that in the presence of the divalent ion, the contribution of the diffuse layer would be negligible. This semi-empirical approach was refined by Shainberg and Kemper[32,33] through their theoretical analysis of the forces acting on the cations in close proximity to the exchanger surface. According to Deshpande and Marshall[34] and Gast[35], ions in the Gouy layer can move about twice as freely as ions in the Stern layer. The distribution between these layers will depend upon (i) surface charge density of the exchanger, (ii) size and valence of the ions, and (iii) probably the fraction distribution of each ion species in the adsorbed layer. Since sodium ions are strongly hydrated, they have a large effective size and, therefore, are not an appreciable part of the Stern layer, so that the effect of the Stern layer on the calculated f_{Na} is much less than on f_{Ca}. Because of the difference in the equivalent volume of the hydrated Ca and Mg ions, Ca must be slightly preferred over Mg. Bower[36] reported that Mg can be made more easily exchangeable than Ca. The greater the Mg saturation, the greater is the preference for Ca. These results were also borne out by the study of Gheyi and van Bladel[37]. Studies conducted by Poonia and Talibudeen[26] on Na-Ca exchange equilibria in some soils from semi-arid tropics and temperate regions (low and high in organic matter) showed that the thermodynamically calculated values of f_{Na} decreased gradually to 1 with increase in Na saturation to 100%. This anomalous behaviour was explained on the basis of the effect of exchangeable Na on the expansion of the clay lattice. The 2:1 clay minerals possess external (freely accessible) and internal (restricted) exchange sites. The increased Na saturation increases the C-spacing[35], and hence makes the internal exchange sites comparatively easily accessible to the solution cations. In Ca sturated soil, at lower Na saturation, the solution Na ions cannot freely compete with Ca ions in the internal (restricted) exchange sites. This yields lower quantities of exchangeable Na for a given equivalent Na fraction in the equilibrium solution, which for all freely accessible exchange sites would be higher. The average value of exchangeable Na (i.e. for internal and external exchange sites) at lower Na saturation gives the impression that Na is excluded by the exchanger or is more loosely bound, which actually is not true. Thermodynamically calculated values of activity coefficients of adsorbed ions should be meaningful for exchangers whose geometry is not influenced

by cation saturations. Hutcheon[24] also observed an anomalous behaviour for the values of f_K in Ca-K exchange, but he tried to explain it on some other grounds.

Since the thermodynamic approach discussed above does not take into account the physical nature of the exchanger, the calculated results with respect to the binding strength of a cation may be misleading. For example, in illitic soils, the calculated value of the binding strength of K^+ will be more than that of Ca^{2+} or Mg^{2+}. This is not because of the long range electrostatic force, but because of the physical trapping of the cation.

Hysteresis or Irreversibility in Exchange Equilibria

There is sometimes hysteresis, i.e. the shape of the exchange isotherm observed when cation A is substituted by cation B is rarely identical to the shape when B is replaced by A. In general, the equivalent fraction of a cation on the exchange complex corresponding to its given equivalent fraction in the equilibrium solution is more when the exchanger is initially saturated with this cation. Tabikh *et al.*[39] explained it on the basis of lack of true equilibrium during the exchange, since any treatment which increases the aggregation of the particles in clay suspension leads to increase in the apparent irreversibility of the exchange. A similar opinion was expressed by van Bladel and Laudelout[21] for $NH_4 \rightleftharpoons$ Mg or Ba exchange reaction in Camp Berteau montmorillonite, and by Deist and Talibudeen[18,19] for K⇌Ca exchange reactions in soils. However, for the exchange reaction Na⇌ Mg or Ca, Sinanuwong and El-Swaify[40] observed that for an initially Na saturated exchanger, the equivalent fraction of adsorbed Na for a given equivalent fraction of solution Na was less compared to the initially Ca or Mg saturated exchanger. They tried to explain this behaviour on the basis of the better dispersion of the prepared Na soils, which made it possible for more sites to be exposed, and, therefore, to become more accessible for exchange by the divalent cation. The incomplete replacement of H^+/ Al^{3+} resulting in imperfect Na saturation in a Na soil preparation may cause higher adsorption of divalent cations for a given equivalent Na fraction in the equilibrium solution. van Bladel and Menzel[41] and Maes and Cremers[42] observed a non-stoichiometric exchange behaviour for Na montmorillonite at higher divalent cation saturation. In addition, van Bladel and Menzel[41] found that CEC measured for Na saturated material changes with the equilibrium electrolyte concentration, while it remains constant for Sr. The reason for this lower Na-CEC is probably the hydrolysis of Na at low equilibrium electrolyte concentrations.

The condition for applying the thermodynamic treatment for describing the data is that perfect reversibility exists for the exchange reaction. It means that when true equilibrium is reached, the equilibrium constant for the forward reaction should be numerically equal to the reciprocal of the backward reaction.

Electric Diffuse Double Layer Approach

It can be visualized that the presence of ions in the vicinity of a charged surface in soil may be either due to dissociation of ions from the surface under the influence of the polar water molecules and/or to the presence of soluble salts in the soil-liquid phase. Whatever may be the reason for the ions to be present in the soil solution, these are under the influence of the two main forces, one being the cause of the other. The coulombic electrostatic force attracts and expels the counter-ions and co-ions, respectively, from near the charged surface and tends to bring the system to a state of minimum energy. A diffusive force then arises which while acting in opposition to the coulombic force tends to bring the system towards maximum entropy. The ultimate effect of these forces acting simultaneously, but in opposite directions, is the formation of the electric diffuse double layer of the ions near the charged surface, in which configuration the system has minimum free energy.

For the sake of simplicity, an infinitely extended, planar negatively charged surface is considered. It is assumed that the distribution of the mobile positive ions in the neighbourhood of the surface (the diffuse double layer) follows Poisson-Boltzmann second order differential equation in one-dimensional form. Deviation from this one-dimensional form at edges and corners can be neglected, as the plates are very thin in comparison to their length and breadth.

Using Poisson-Boltzmann second order differential equation in one-dimensional form for electrical diffuse double layer, Eriksson[7] derived the following relationship between mono-divalent cations in the equilibrium solution and mono-divalent cations in the diffuse double layer:

$$\frac{\sigma_1}{\sigma} = \frac{e\, n_1^\circ}{\lambda\sigma\sqrt{n_2^\circ}} \sinh^{-1} \frac{(\lambda\sigma\sqrt{n_2^\circ})}{(n_1^\circ + 4V_c\sqrt{n_2^\circ e})} \qquad \ldots(11)$$

where σ_1/σ is the fraction of the net space charge in the diffuse double layer neutralized by monovalent cation; n_1° and n_2° are the number of ions (per cm^3) in the equilibrium solution; e is the electronic charge; λ, is the electrical diffuse double layer constant; V_c is related to the potential at the central plane midway between the clay plates; and σ is the net space charge in the diffused double layer[7].

The above treatment pertains to a system in which the equilibrium concentrations of monovalent and divalent cations are matched precisely by equal concentrations of monovalent and divalent anions. In other words, the treatment is applicable to perfectly symmetrical salts like $M^+ A^-$ and $M^{2+} A^{2-}$. A simplified version of Eriksson's equation[7], as given by Bolt[8], is

$$\frac{\Gamma_1}{\Gamma} = \frac{r}{\Gamma\sqrt{\beta}} \sinh^{-1} \frac{\Gamma\sqrt{\beta}}{r + 4V_c\sqrt{C_2}} \qquad \ldots(12)$$

where Γ_1/Γ is the fraction of surface charge neutralized by a monovalent cation; Γ, the total surface charge density (meq cm^{-2}); $\beta \left(= \frac{8\pi F^2}{1000\, \varepsilon RT}\right)$

with F as the Faraday constant ($2{\cdot}892 \times 10^{11}$ esu me^{-1}); R, the universal gas constant=($1{\cdot}045$ and $1{\cdot}06$) $\times 10^{15}$ cm mmole^{-1} at 6·5°C and 25°C, respectively; and V_c (=cosh Y_c) is related to the potential in the plane midway between the platelets. For most practical purposes, V_c may be taken to be unity, which means cosh $Y_c = 1$ or $Y_c = 0$, i.e. infinite plate distance $r = C_1/\sqrt{C_2}$ (mole$^{1/2}$litre$^{1/2}$). As mentioned earlier, Eq. (12) applies only to symmetrical salts, but it was shown by Bolt and Page[43] that it is sufficiently accurate even for asymmetrical systems in which the mono- and divalent cations are not exactly matched by equal number of anions of the same valence.

It may be inferred from the relationships given by Eriksson[7] and Bolt[8] that a higher charge density would favour the adsorption of divalent cations over monovalent cations. Since the surface area remains independent of pH, the surface charge density increases as the pH and CEC increase. This effect of pH of causing increased Ca adsorption in Na-Ca exchange equilibria was reported by Pratt *et al.*[44]. Similar results were obtained by Schalscha *et al.*[45] in their study on K-Ca exchange equilibria in volcanic-ash soils.

While interpreting the experimental data, most of the workers have reported that normally the surface charge density in Eq. (12) is to be multiplied by an empirical factor to make it fit the experimental data. For Na-Ca exchange, this factor was reported to be 1·2 for illite[8], 1·4 for some arable soils and montmorillonite[36], 1·0-2·1 for some acid soils[44] and 1·3-4·6 for some temperate and semi-arid tropical soils varying in surface charge density and organic carbon content[26].

The large variations in the correction factors for the surface charge density necessary to make the experimental data fit the equation suggest that either there is something inherently wrong with one or both of the experimental determinations that lead to the values of the surface charge density or the soils have rather wide differences in the specificity with which they adsorb Ca vs Na ions, which are independent of the effect of surface charge density. It is possible that various minerals present in the clay fractions, such as quartz, feldspar and amorphous oxides of Fe, Al and Ti contribute to the surface area without adding much to CEC. Also, certain organic colloids might contribute in a similar manner. Peigneur *et al.*[46] also reported that normally the surface charge is not uniformly distributed, but is confined to areas of high and low charge densities. They could predict the experimental differences in behaviour reasonably well in their study of cobalt adsorption on montmorillonite using a model comprising two areas of different charge densities.

van Bladel *et al.*[47] could not find reasonable agreement between the experimental results and the theoretically calculated ones, even after multiplying the measured surface charge density by an appropriate factor. On the basis of their results on Na-Ca montmorillonite, they reported that the calculations based on the theory of the electric double layer on a planar surface fit the experimental data much better if one takes into account the interaction of the surface of clay particles by choosing a value at 25°C for the dimensionless potential, Y_c, midway between the platelets as 4, 3·5 and 3 at 5, 10 and 25 meq litre^{-1} total salt concentrations, respectively.

Relationship between Thermodynamic and Diffuse Double Layer Treatments

Laudelout *et al.*[20] presented an elaborate treatment based on a hypothetical discharging or charging procedure as used in the derivation of the Debye-Huckle equation, which allowed one to calculate the limiting value of the coulombic contribution to the free energy of exchange. Their equation is

$$\Delta G^\circ \text{ Coul. } (C_o \longrightarrow 0) = RT\left(1 - 1n\,\frac{\Gamma\sqrt{\beta}}{2}\right) \quad ...(13)$$

Using the theory of diffuse double layer, van Bladel *et al.*[47] also tried to calculate the values of the coulombic selectivity-quotients K_C' (Coul.) in Na-Ca montmorillonite system. They used the following equation:

$$K_C' \text{ (Coul.)} = \frac{\Gamma\ (\Gamma\beta - r\sqrt{\beta}\ \sinh^{-1} Z)}{(\sinh^{-1} Z)^2} \quad ...(14)$$

$$\text{with } Z = \Gamma\sqrt{\beta}/(4\ V_c\sqrt{C_o^{++}})$$

By integrating the values of $1nK_C$ over the whole range of the exchange isotherm for mono-divalent cation pair and using Eq. (11), the values of the coulombic thermodynamic exchange constant $1nK_{Coul.}$ were obtained at finite electrolyte concentration. By extrapolating the values of $1nK_C$ to vanishing ionic strength, the coulombic component of the thermodynamic exchange constant and the standard free energy of exchange (Eq. 2) were obtained. Although the two independent approaches are based on the same distribution pattern of the ions according to the Gouy theory using freely expanded double layers, they showed good agreement. This reveals that Eriksson's simplified approach is good enough for all practical purposes.

Empirical Approach

The most extensively used empirical exchange equation dealing with cation exchange equilibria is due to Gapon[4]. Following the convention introduced by Gapon in specifying concentration (C_o^+ and C_o^{2+}) in mole litre^{-1}, this equation is written as

$$\gamma^+/\gamma^{2+} = K_G\,\frac{C_o^+}{\sqrt{C_o^{2+}}} \quad ...(15)$$

where γ^+ and γ^{2+} refer to monovalent and divalent cations on the exchanger and K_G is the Gapon constant. Evidently, K_G has the units mole$^{-1/2}$ litre$^{1/2}$.

The relationships between exchangeable sodium percentage (ESP) and sodium adsorption ratio (SAR, Na / $\sqrt{\text{Ca+Mg}}$, with ion concentrations in mmoles/litre)[13] can be related with the Gapon constant (K_G) as under:

$$\text{ESP} = \frac{100\ K_G\ (\text{SAR}\sqrt{1000})}{1 + K_G\ (\text{SAR}\sqrt{1000})} \quad ...(16)$$

For soils containing illite as the predominant mineral, the value of K_G is roughly 0·5 for Na-Ca exchange.

Eq. (16) thus becomes

$$ESP = \frac{100 \times 0{\cdot}015\ SAR}{1 + 0{\cdot}015\ SAR} \qquad ...(17)$$

Eq. (17) is identical with the empirical relationship based on the data of 81 soil samples analysed at the US Salinity Laboratory[13]. The type of clay mineral plays an important role in influencing the value of the Gapon constant. Plots between SAR and ESP for the various values of Gapon constant as calculated from Eq. (17) and from the empirical relationship worked out in the US Salinity Laboratory[13] are shown in Fig. 3.

Based on the experimental results on bentonite clay, soils and synthetic resins, Krishnamoorthy and Overstreet[6] reported that Gapon equation was unsatisfactory/wholly inadequate for mono-divalent/mono-trivalent cation exchange. They observed that with increase in Cs saturation from 15 to 66% on exchange in Ca-Cs bentonite system, the value of K_G increased from 5·05 to 8·8, while in La-Cs bentonite system, K_G increased from 1·3 (12·5% Cs) to 5·2 (17·5% Cs). Similar variations in the value of K_G for montmorillonite system for Ca-Na exchange have been reported by van Bladel *et al.*[47], above about 20% Na saturation. Contrary to this, some workers[26,36,37] observed that the value of K_G remains fairly constant at least up to 40-50% Na saturation. Even in the case of resin (Dowex-X4, CEC 4·66 meq g^{-1}), K_G was found to be fairly constant up to 40% exchangeable Na[48].

The value of K_G, which determines the preference of one cation to another in a given system, not only depends upon the type of the aluminosilicate mineral predominantly present in the soil, but it may also be affected by $CaCO_3$ and the organic matter present in the soil. Gheyi and van Bladel[37] observed an average difference of about 30% in the value of K_G for calcareous and $CaCO_3$-free soils, indicating relatively higher preference for Ca in the former. However, from their experimental procedure, it appears that it is not the removal of $CaCO_3$ which increases Na selectivity, but lowering of the *p*H of soil with acetic acid treatment (at *p*H 3) while removing $CaCO_3$, which, in turn, reduces the CEC/surface charge density of the soil. Treatment of even a non-calcareous soil with acetic acid, resulting in lowering of soil *p*H, would probably have a similar effect on ion selectivity/Gapon constant. The results of this investigation suggest that the stress given on the effect of $CaCO_3$ on soil *p*H seems to be unwarranted, because soils free from $CaCO_3$ may also have a high *p*H. Poonia and Talibudeen[26] observed a marked effect of organic carbon content and/or surface charge density of soils on the values of K_G. For Ca-Na exchange, this value was found to be negatively related to these two parameters. Further, K_G remained fairly constant up to about 50 ESP for all the 26 soils tested. This behaviour is in accordance with the theory of ion exchange selectivity involving surface charge density.

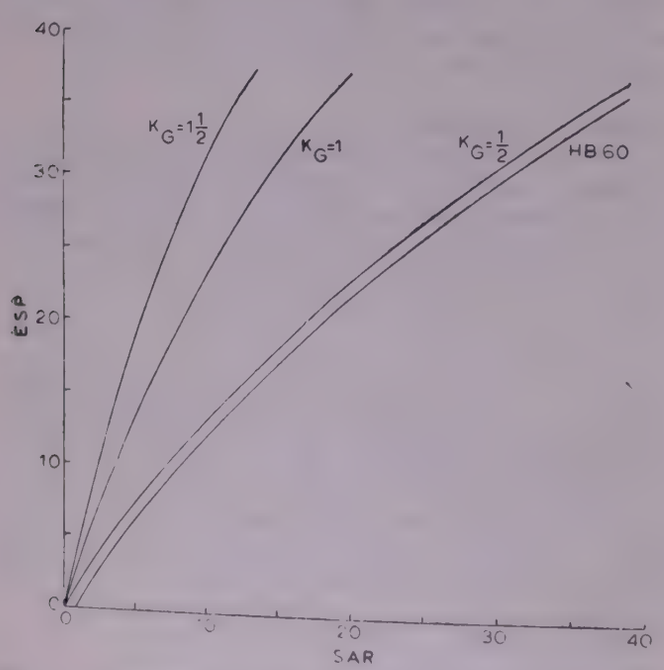

Fig. 3 — Relationship between exchangeable sodium percentage (ESP) and sodium adsorption ratio (SAR) for different Gapon constants

Schalscha *et al.*[45], from their study on volcanic ash soils, reported that with increase in potassium saturation percentage (especially beyond 10%) and/or increase in *p*H, the value of K_G decreased, showing a relatively low affinity for K at high K saturation and/or high *p*H. A critical examination of the results of these workers reveals that beyond 10% K on exchange (presumably preferential/K fixing exchange sites) in volcanic ash soils, the remaining exchange sites are non-preferential for either cation. The effect of *p*H on the value of K_G is obvious, as the *p*H causes increase in CEC (without changing the surface area) and hence the surface charge density. Similar results with regard to the effect of K saturation on the value of K_G have been reported by Bolt *et al.*[49] for illitic soil, and Carson and Dixon[50] for soils in general.

Lagerwerff and Bolt[51] tried to relate Eriksson's equation with the empirical approach of Gapon as under:

$$\frac{\gamma^+}{\gamma^{++}} = \frac{\dfrac{1}{\sqrt{\beta}} \sinh^{-1} \dfrac{\Gamma\sqrt{\beta}}{\gamma + 4V_c\sqrt{a^{++}}}}{\Gamma - \dfrac{r}{\sqrt{\beta}} \sinh^{-1} \dfrac{\Gamma\sqrt{\beta}}{r + 4V_c\sqrt{a_o^{++}}}} r \qquad ...(18)$$

Or

$$\frac{\gamma^+}{\gamma^{++}} = Kr \qquad ...(19$$

where $\gamma^+ = S\Gamma_+$, $\gamma^{++} = S\ \Gamma_{++}$, with S as the specific surface area and $r = a_0^+/\sqrt{a_0^{++}}$, with a_0^+ and a_0^{++} as the activities of monovalent and divalent cations in the equilibrium solution. They determined the deviation of the values of K obtained according to Eq. (19) using the experimental data, from the value obtained using Eq. (18). The deviation was used to estimate the specific adsorption energies to which the ions were being subjected. The agreement in the

case of montmorillonite and the disagreement in the case of illite between the theoretical and the experimental values of the exchange factor in Gapon equation pertaining to a system containing K and Ca, stress the fact that in the build up of the double layer, valence forces are predominant in the case of montmorillonite and specific adsorption forces in the case of illite.

Statistical Thermodynamic Approach

The charge on the colloid may be due to substitution, dissociation of surface groups or the preferential adsorption of anions. Thus, the charges may arise at specific points and the adsorbed ion may be associated with a particular adsorption site. This model, introduced by Davis[5], Davis and Rible[52], Krishnamoorthy *et al.*[53], and afterwards applied to exchange on soils, clays and resins by Krishnamoorthy and Overstreet[6], is based on the assumptions that (i) the adsorbed ions are localized and one layer of ions would neutralize the surface charge, (ii) the neighbouring ions have no influence on the interaction energy of an ion and the site, and (iii) the distance between the sites is large compared to the ionic size.

The generalized equation from this model, suggested by Krishnamoorthy *et al.*[53] and Davis[5], is

$$K_D = \frac{M_{Be}^{nBe}}{M_{Ae}^{nAe}\left(\sum_i q_i M_i e\right)^{nBe-nAe}} \cdot \frac{a_A^{nA}}{a_B^{nB}} \quad \ldots(20)$$

$$= \text{Constant},$$

where q is a parameter whose value depends on the valence of the ion and the assumed number of the nearest adsorption sites (Y), to the given adsorption site[5]. q_i for any adsorbed ion i of valence Z is given by:

$$q_i = \frac{YZ_i - 2Z_i + 2}{Y} = Z_i - \frac{2Z_i}{Y} + \frac{2}{Y}$$

For example, for a monovalent-divalent case

$$q_+ = 1 \text{ and } q_{++} = 2\left(\frac{Y-1}{Y}\right)$$

Various exchange equations may be derived from the above generalized equation by assigning different values to Y. For $Y = 2$, i.e. linear array of surface charges, $q_i = 1$, then

$$K_D = \frac{a_A^{nA} M_{Be}^{nBe}}{a_B^{nB} M_{Ae}^{nAe}} = \text{Constant}$$

$$= K_V \quad \ldots(21)$$

where K_V is Vanselow constant.

Bloksma[54] pointed out that in selecting a hexagonal array (Y=6) of surface charges, there are eight adjacent sites for a divalent ion; two of these sites give the value of $q^{++} = 4/3$, rather than 5/3. Hence,

$$K_D = \frac{a^{++}}{a^{+2}} \cdot \frac{M^{+2}}{M^{++}(M^{+}+1{\cdot}6M^{++})} = \text{Constant} \quad \ldots(22)$$

It is evident from Eq. (22) that as the number of exchange sites closer to a given adsorption site increases, the value of the selectivity coefficient (K_D or K_{KDO}) for Ca-Na exchange decreases gradually, exhibiting less preference for Na. However, the rate of decrease in the preference for a monovalent cation is not in proportion to the increase in the number of influencing exchange sites. This is in consonance with the cation exchange equation (Eqs. 11 and 12) based on electrical diffuse double layer theory[7], which also predicts increased preference for a divalent cation with increase in the surface charge density of the exchanger.

Krishnamoorthy and Overstreet[6], while working on bentonite clay, soils and resins, observed that for explaining experimental data on cation exchange, the statistical thermodynamic approach (based on Guggenheim theory, Eq. 20) was much better than the other empirical approaches like that of Vanselow and Gapon. However, Pal[48], while working with a resin (Dowex X-4), observed that the selectivity quotients based on statistical thermodynamic theory, Vanselow equation and Eriksson equation are fairly constant for a wide range of exchangeable Na in a Ca-Na exchange system.

It is important to note that the selectivity of a cation is markedly influenced by the associated anion in the system. For a Ca-Na soil system, Babcock and Schulz[55] observed a higher value of the Vanselow coefficient, K_V (Eq. 21) for the SO_4^{2-} system than for the Cl^- system, thus giving higher ESP in the former case. However, the difference in the values of K_V in the two systems was narrowed down by considering ionic activities rather than their concentrations. The activity coefficients in mixtures of Na_2SO_4 and $CaSO_4$ as a function of ionic strength were estimated by calculating the thermodynamic solubility product from the standard free energies given by Latimer[56] and using the solubility data for gypsum given by Seidell[57]. Rao *et al.*[58], however, observed a more satisfactory agreement for their results in Cl^- and SO_4^{2-} systems, when the activity coefficients were calculated taking into consideration the ion pair formation of SO_4^{2-} with Ca and Mg. While recalculating the values of different selectivity coefficients (K_V, K_D, K_E and K_G) from the experimental data of Babcock and Schulz[55], Van Beek and Bolt[59] found that the values of K_s agreed well for SO_4^{2-} and Cl^- systems when the refinement suggested by Rao *et al.*[58] in the form of ion pair formation was considered.

Approach Based on Ion Distribution in Diffuse Double Layer

An attempt was made by Heald *et al.*[31] to develop a semi-empirical approach to predict exchangeable cation, considering the distribution of adsorbed ions over the Stern and the Gouy parts of the diffuse double layer. For a mono-monovalent ion exchange system (A-B), their equation, in the simplified form, is

$$q_A = K' q_A (C_B - C_A) + 1 + (\Gamma_G/\Gamma) \frac{(C_B/C_A)(K'-1)}{1 + (C_B/C_A)} \quad \ldots(23)$$

where q_A is the equivalent ion fraction of the adsorbed A; C_B and C_A are the equivalent ion fractions of solution B and A; Γ_G is the exchangeable cation in the Gouy layer; Γ, the total surface charge; and K' (the selectivity factor) is defined as K_B/K_A, K_B and K_A being the ion pair formation constants between these ions and the surface charge.

Donnan Equilibrium-Ratio Law

A generalized theory concerning the state of equilibrium of a system containing a membrane impermeable to one ion species was formulated and extended by Donnan[60] and Donnan and Guggenheim[61]. Studies have indicated that any system in which at least one ion species is restrained from freely diffusing throughout the whole system is also characterized by a Donnan distribution. For example, layer silicates (clay particles with their surrounding diffuse double layer) may be looked at as a micro-Donnan system[62,63], where the attractive electric forces between the particle surface and counter-ions act as a restraint, causing non-uniform distribution of the counter-ions in the micellar solution. Thus, two solution phases are recognized, micellar and intermicellar, over which the cations are distributed. The standard states of the cations in the two solutions may be chosen in the same way as done by Gaines and Thomas[9].

At equilibrium, the electrochemical potential of any ion in the two phases, the micellar phase denoted by superscript m, and the intermicellar phase by superscript i, should be equal. Thus, for a monovalent cation shown by the subscript +,

$$RT \ln (a_+^m / a_+^i) = - F (\psi^m - \psi^i) \quad ...(24)$$

Similarly, for a divalent cation,++,

$$\tfrac{1}{2} RT \ln (a_{++}^m / a_{++}^i) = - F (\psi^m - \psi^i) \quad ...(25)$$

where F is the Faraday constant; and ψ, the electrical potential. Since the RH sides of Eqs. (24) and (25) are equal, one gets,

$$\frac{a_+^m}{a_+^i} = \left(\frac{a_{++}^m}{a_{++}^i}\right)^{\frac{1}{2}} = \left(\frac{a_{+++}^m}{a_{+++}^i}\right)^{1/3} \quad ...(26)$$

Eq. (26) is not similar to Schofields[64] ratio law, according to which, when cations in a solution are in equilibrium, with a large number of exchangeable ions, a change in the concentrations/activities of the solution will not disturb the equilibrium, if the concentrations/activities of all the monovalent ions are changed in one ratio, those of all the divalent ions with square of that ratio and those of all the trivalent ions in the cube of that ratio.

Conclusion

The predictive approaches discussed may be used to ascertain the degree of preference an exchanger shows for a particular cation and/or the composition of exchange complex in equilibrium with a given solution.

The thermodynamic treatment enables one to know the relative preference of the exchanger for one cation over another. The changes in the composition of the exchange complex with respect to the changes in the equilibrium solution cannot be predicted on the basis of this treatment. Further, the activity coefficients of the adsorbed ions fail to give quantitatively the binding strength of a particular cation in absolute terms; they simply give the relative exchangeabilities of cations at their different degrees of exchanger saturation.

The diffuse double layer approach, besides accounting for the preference of an exchanger for a particular cation, predicts the composition of an exchanger in equilibrium with a given solution. However, the strength and the weakness of this theory lie in the introduction of the surface charge density (SCD), which determines the preference of one cation over another. The lower the SCD of the exchanger, the higher is its preference for a monovalent cation. Apart from the usual errors in the experimental determination of the SCD, it gives only an average value without any regard to its heterogeneity, i.e. zones of high and low SCD.

The purely empirical and semi-empirical or statistical thermodynamic approaches propounded to explain the experimental results are free from involved mathematical considerations/assumptions and are simple to use. They not only give the relative preference of a cation by an exchanger (based on selectivity quotients) but can also predict the changes in the cationic composition of the exchanger. For Na-Ca exchange, the statistical thermodynamic exchange coefficient remains fairly constant over a wide range of Na saturation, while the most widely used Gapon equation fails when the soil ESP goes beyond 40-50. Its applicability is further limited to 20-30 ESP for montmorillonitic clays and resins.

None of the predictive approaches can take into consideration all the complexities of a soil system. The specific adsorption of cations, the non-uniform distribution of charge on the exchange surface, the geometric variations in the aluminosilicate minerals as influenced by *p*H and cationic saturation, non/partial reversibility of exchange, formation of organo-mineral complexes need to be probed further to improve the utility of these approaches in enabling the prediction of changes in cationic compositions under specific situations.

Summary

A critical review of the various predictive approaches, viz. thermodynamic, electrical diffuse double layer theory, empirical and semi-empirical (statistical thermodynamics) used in cation exchange equilibria in soils is attempted. The theoretical background along with the applicability of these approaches to experimental results on soils/clays/resins for different cation pairs, obtained by different workers, have been critically examined and discussed. The merits and demerits of these approaches with regard to their ranges of applicability are given. A brief description is given of the methodology adopted in cation exchange equilibria studies and its shortcomings are pointed out.

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Adaptive Changes to Survival during Aestivation in the Gastropod Snail, *Pila globosa*

K. S. SWAMI & Y. SRINIVASA REDDY
Department of Zoology, Sri Venkateswara University, Tirupati 517 502

AESTIVATION is a usual but enigmatic phenomenon resorted to by several gastropods of the tropical countries wherein the animal survives the dry seasons by burrowing itself deep into mud layers and remains without food, water and oxygen until the advent of rains. In nature, the period of aestivation lasts 3-4 months, but in the laboratory the animal survives for periods as long as 3-4 years. Such a physiological state involves the rates, and directions of metabolic reactions so adjusted that there is a metabolic homeostasis in the changed environment.

Biology of *Pila globosa*

The Indian apple snail, *Pila globosa*, inhabits ponds, streams and paddy fields and feeds on aquatic vegetation. The mantle cavity is divided into a gill chamber and pulmonary sac. The gill chamber meets the respiratory requirements when the animal is submerged in water. When the water gets foul or insufficiently aerated, the animal resorts to aerial respiration, recruiting the pulmonary sac for aid. When the water gets dried up in smmer, the animal retires into the deeper layers of mud, withdrawing the body into the shell and tightly closing the operculum. *Pila* can remain in this apparent state of suspended animation for long periods until the onset of rains. In the laboratory, the animals were found in this torpid state for 3-4 years and they were found to revive within a few hours and lived normally when placed in water.

Aestivation : Aerobic or Anaerobic

There are two different schools of thought concerning the oxygen dependency of the snails during aestivation. Prashad[1] believed that *Pila* makes use of the air stored in the pulmonary sac during aestivation and that carbon dioxide escapes out in the form of bubbles when the animal is made to revive in water. But Meenakshi[2] doubted whether the small amount of air trapped in the pulmonary sac can meet the respiratory requirements of the animal during the whole period of aestivation, which may continue from months to years. She[3] showed that the gas escaping out from the revived animal is an inert gas, probably nitrogen but not carbon dioxide. By using mercury manometers[4], the shell is shown to be impervious to gases and the closure of the operculum is too tight to allow any gaseous exchange. Based on these studies and on the ability of the snail to survive in plastimold for 3 months, she gave the opinion that respiration in the snail is a peculiar type of anaerobiosis, divesting itself from the conventional Pasteur's effect. However, later studies involving administration of ^{14}C glucose and trapping of the evolved $^{14}CO_2$ indicated that the snail, *P. globosa*, could be partially aerobic[5]. A similar pattern was suggested by Coles[6] in the aestivation of *P. ovata* and *Bulimulus nasutus*, where the aestivated snail needed about 17% of the oxygen requirement of active snail. Thus, it appears that the snail is capable of partial anaerobic existence tolerating different degrees of oxygen tension. Meenakshi[4] suggested that the increased calcium levels in blood buffers the elevated lactate levels, thus regulating the blood *p*H and averting acidosis. However, Ramana Rao[7] observed that the buffering capacity of blood protein, especially of the α-amino and guanidine groups increases significantly on the alkaline side of the homogenate *p*H in aestivating *P.globosa*, which provides an efficient buffering potential against secreted internal metabolic acids. Srinivasa Reddy[8] showed that the tissues of aestivating *Pila* resorted to variable degrees of anaerobiocity as evidenced by variable lactate contents and glycogen depletion. The mantle tissue immediately below the shell is supposed to be relatively aerobic compared to the inner core of the tissues in the snail. Since the heart beat and blood circulation decreased considerably[9], even the limited available oxygen could not be transported to the interior tissues, while the mantle, by virtue of its location immediately beneath the shell, has the advantage of trapping the external oxygen directly. The shell may be less permeable to gases and this restriction on gaseous exchange may act as a safety valve to reduce the dehydration hazards.

Factors Inducing Aestivation

Hibernation and aestivation are believed to be passive responses to environmental influences[10] which may result in the dehydration of the animal, as evidenced by the depression in the osmotic pressure[11] and loss of water in dormant snails[12]. But in the aestivating *Pila*, the tissue water content does not change[13] Meenakshi[3,4] believed that the drop in humidity of the environment is the main factor inducing aestivation in *Pila virens* and the aestivation metabolism is under the influence of a steroid hormone produced by the neurosecretory cells in the cerebral ganglia. The drop in the humidity of the environment is supposed[14] to activate the neurosecretory cells in the cerebral ganglia either by the transduction of the environmental stimuli in the peripheral hygroreceptors to become nerve impulses, which are carried to the cerebral ganglia to be transduced into hormonal messages by the neurosecretory cells[15] or by the transduction of the environmental signals directly in the neurosecretory cells without the intervention of a nerve impulse[16]. Thus, activated neurosecretory cells secrete a steroid hormone which is directly involved in the aestivation effects. By injecting aqueous ether and alcohol extracts of the cerebral ganglia of aestivating *Pila* into active *Pila*, an increase in calcium and magnesium levels is brought about and respiration is lowered. A 10-fold rise in the sterol content of the brain of *P. virens* and rise in the blood calcium and magnesium levels during aestivation suggest that the steroid hormone might be the possible candidate responsible for inducing aestivation. Elevation in the levels of acidic amino acids in the body fluid and

tissues of aestivating *P. globosa* has been reported[7,17]. Acidic amino acids have been found to have an inhibitory effect on the electrical activity and the action of different enzymes in the metabolism.

Electrical and acetylcholinesterase activities — The general pattern of electrical activity in normal and aestivated animal tissues indicates the prevalence of a different metabolic pattern in the aestivating

TABLE 1 — ANALYSIS OF SPONTANEOUS ACTIVITY IN DIFFERENT NERVES IN NORMAL AND AESTIVATED *P. globosa*

Nerve	Normal		1 month		2 months		3 months	
	No. of spks/sec	No. of spks categories	No. of spks/sec	No. of spks categories	No. of spks/sec	No. of spks categories	No. of spks/sec	No. of spks categories
Cerebral commisure	73	5	57	2	31	1	18	1
Cerebropedal connective	92	7	67	4	48	3	39	1
Cerebropleural connective	77	7	58	2	38	2	Nil	Nil
Infraintestinal nerve	91	12	69	4	61	2	Nil	Nil
Supraintestinal nerve	82	9	48	2	27	1	21	1
Left pleurovisceral connective	120	11	75	7	28	2	19	2
Right pleurovisceral connective	81	3	31	2	16	1	Nil	Nil
Osphradial nerve	77	4	45	4	27	4	8	1

Fig. 1 — Spontaneous activity recorded from the infraintestinal nerve [Note the decrease in amplitude and frequency of pulses on aestivation. N, normal snail; (1) 1 month aestivated snail; (2) 2 months aestivated snail; (3) 3 months aestivated snail; time, 0.4 sec; and Calib: 400 μV]

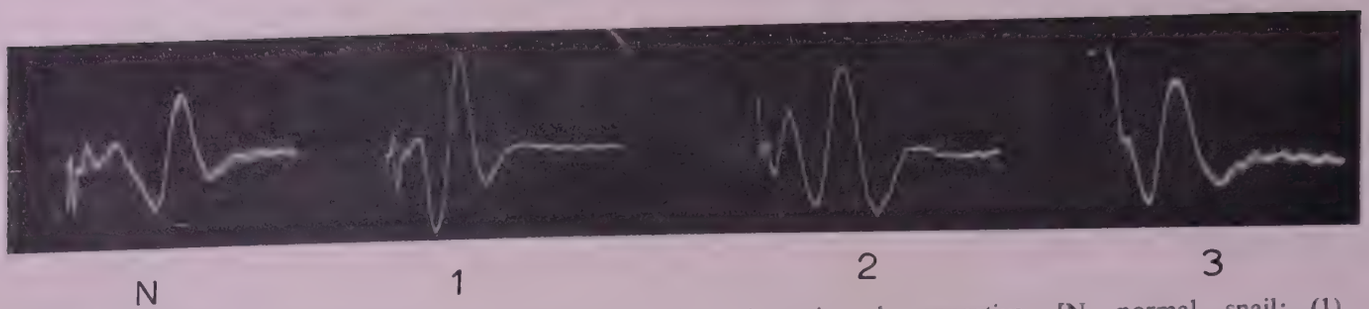
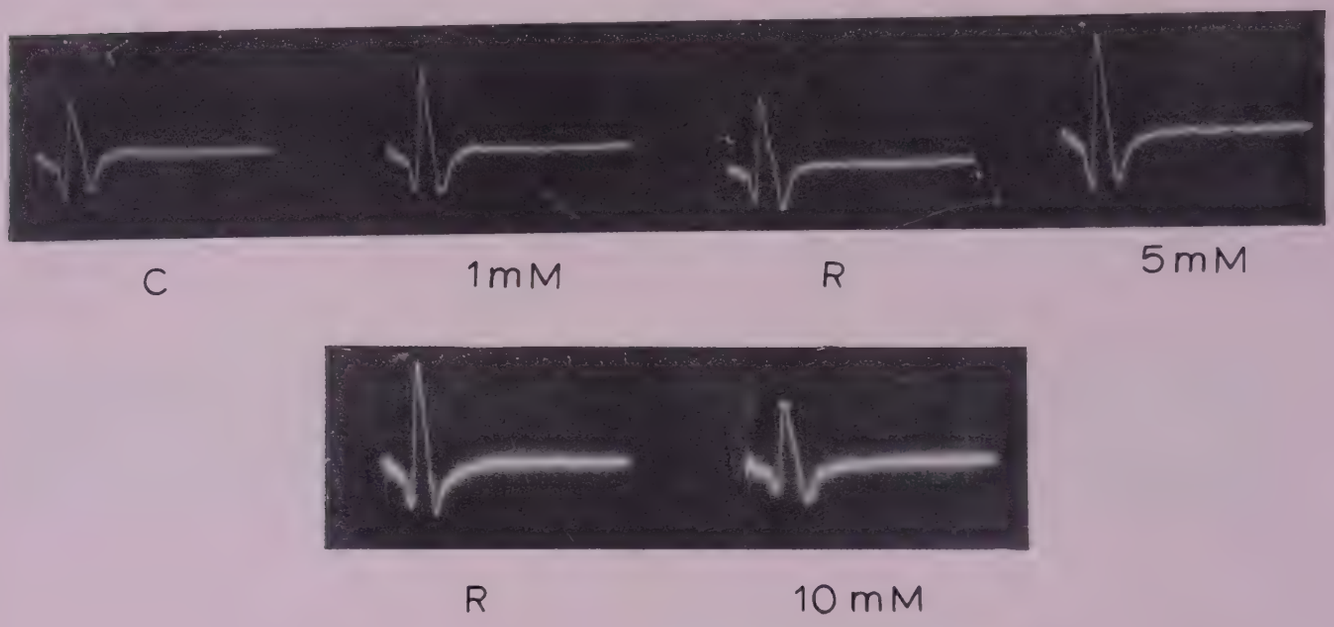


Fig. 2 — Stimulation of osphradial nerve and recording from left pleurovisceral connective [N, normal snail; (1) 1 month aestivated snail; (2) 2 months aestivated snail; (3) 3 months aestivated snail. Note the absence of faster responses on aestivation; calibration time, 20 msec; amplitude, 200 mV]



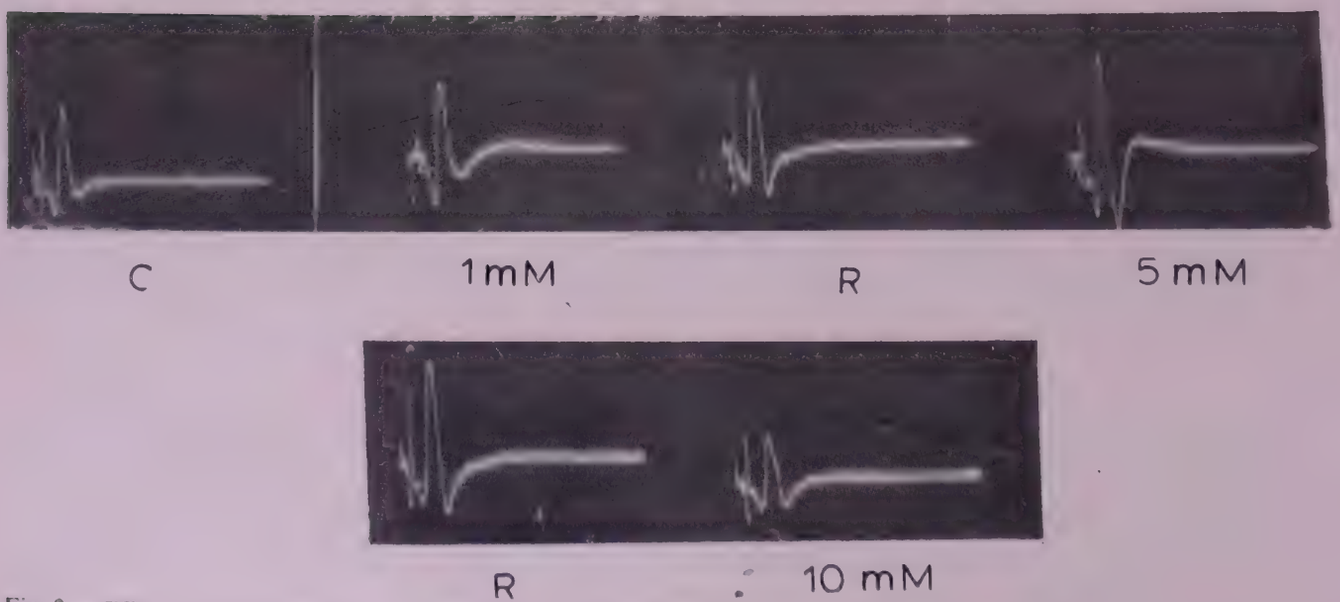


Fig. 3 — Effect of glutamic acid at 1, 5 and 10 m*M* concentrations on the responses to electrical stimulation of the left pleurovisceral connective of active (a) and aestivated (b) *Pila* ['R' represents the revival on treatment with ringer after treatment with each concentration of the amino acid. A stimulus strength of 6V was applied. Note the gradual decrease in amplitude; time, 50 msec; amplitude, 200 mV]

animal as compared to the normal ones. The glutamic acid dependent metabolic inhibition predominates in aestivation.

The electrical activity of different nerve connectives and commisures during aestivation was studied by Murali Mohan[17]. The spontaneous activity decreased in all the nerves on aestivation and this decrease was characterized by lowered amplitudes and frequencies of the action potentials and also a drop in the number of spike categories[17] (Figs 1-4). The decrease in the spontaneous electrical activity was progressive with the aestivation period, reaching very low levels in certain nerves and getting totally silent in other nerves at the end of 3 months of aestivation.

When different nerves were stimulated, only the slow moving components were found to persist, while the

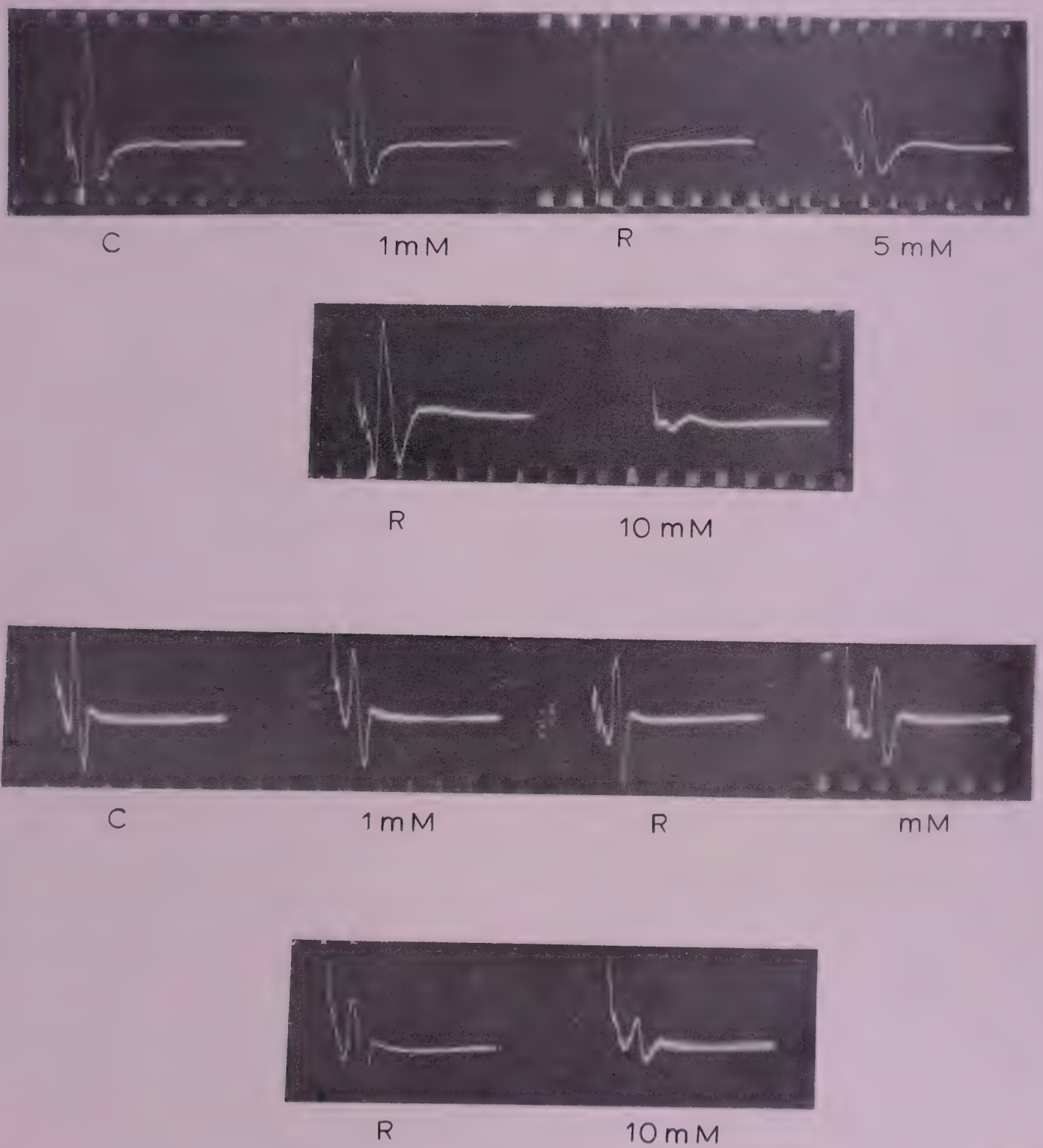


Fig. 4 — Effect of arginine at 1 , 5 and 10 m*M* concentrations on the responses to electrical stimulation of the left pleurovisceral connective of active (a) and aestivated (b) [Note the increase in spike amplitude on treatment with concentrations and the gradual decrease at 10 m*M* concentration of the amino acid; time. 50 msec; amplitude, 200 mV]

fast moving components became silent in snails aestivated for 3 months. This ceasure of firing of fibres with greater conduction velocities was achieved gradually, since in the snails aestivated for 1 and 2 months the fast fibres still continue to fire. This persistence of electrical activity indicates that the alertness of the animal was not lost immediately after the snail was made to aestivate. As the aestivation progressed, the animal slowly settled down with the torpid state and retained only the slow responses and suppressed the faster ones. The drop in the alertness of the snail was evident also from the gradual increase in the threshold voltages and decrease in the conduction velocities of all the nerves during aestivation (Tables 2 and 3). Congruent with the loss of electrical activity, a decrease in acetylcholinesterase activity was observed during aestivation in the nervous tissue of *P. globosa*[18]. During the first month of aestivation, the decrease in the electrical response and acetylcholinesterase activity was sharp, followed by further drops in the levels in the second and third months.

Contrary to the nervous system, the acetylcholinesterase activity was found to increase in other tissues like foot, mantle, gut and hepatopancreas of aestivated *P. globosa*. It appears that the lowered nervous control on the innervated tissues results in a compensatory hyperactivity of acetylcholinesterase in the tissues.

When the general alertness of the animal tissues decreases, showing lowered physiological activity, the energy demands should also decrease and the glycolytic and oxidoreduction systems could be altered.

Glycolysis — Glycogen decreases (Table 4) in all the tissues of the snail during aestivation but it is not totally depleted lest it should disrupt the enzymes associated with the glycogen particles[19]. This may be due to the finesse of control by phosphorylase, which feeds glycogen into the glycolytic pathway[20,21]. In contrast to the phenomenal increase in other glycolytic enzymes, it shows only a moderate rise in activity in the tissue of aestivated snails.

The decrease in glycogen content during aestivation must be proportional to the lactic acid increase, since the animal is living in an oxygen-free environment and the possibilities of glycogen being broken down to carbon dioxide and water are remote. But the lactic acid content in hepatopancreas and mantle in aestivated snails is less than in the active snails and the moderate increase in lactic acid in the foot does not account for the decrease in glycogen content (Table 4). The lactate dehydrogenase activity is also very low (Table 4) in all the tissues of both active and aestivated snails. Similar reports were made in facultative

TABLE 2 — CONDUCTION VELOCITIES IN DIFFERENT NERVES IN NORMAL AND AESTIVATED *P. globosa*

Nerve	Normal	Aestivated		
		1 month	2 months	3 months
Cerebral commissure	12·5	11·3	9·8	8·6
Supra intestinal nerve	51·5	36·0	Absent	Absent
	19·5	12·8	10·5	9·0
Osphradial nerve	16·1	12·8	11·2	9·6
Left pleurovisceral	88·1	Absent	Absent	Absent
connective	60·5	58·5	38·1	30·5
	43·1	24·0	18·8	16·9
Osphradial left	176·0	Absent	Absent	Absent
pleurovisceral	42·7	33·5	31·5	Absent
	12·5	11·5	9·7	8·0
Right pleurovisceral	76·6	55·2	30·4	Absent
	31·0	24·3	15·2	11·1

TABLE 3 — THRESHOLD VOLTAGES OF DIFFERENT NERVES IN NORMAL AND AESTIVATED *P. globosa*[17]

Nerve	Normal	Aestivated		
		1 month	2 months	3 months
Cerebral commissure	4·3	5·5	6·0	8·0
Supra intestinal	4·1	5·0	Absent	Absent
nerve	4·9	5·8	6·2	7·4
Osphradial nerve	4·6	5·3	6·1	6·9
Left pleurovisceral	2·5	Absent	Absent	Absent
connective	2·8	3·0	3·1	3·4
	3·0	3·2	3·4	3·6
Osphradial to left	2·0	Absent	Absent	Absent
pleurovisceral	3·0	3·5	5·0	Absent
	3·0	3·5	5·0	6·0
Right pleurovisceral	4·0	4·4	4·8	5·3

TABLE 4 — GLYCOGEN, LACTIC ACID AND LACTATE DEHYDROGENASE IN SELECTED TISSUES OF ACTIVE AND AESTIVATED *P. globosa*

Activity	Hepatopancreas		Mantle		Foot	
	Active	Aestivated	Active	Aestivated	Active	Aestivated
Glycogen, mg/g wet wt	3·04	1·46	1·46	0·94	2·83	1·09
Lactate mg/g wet wt	0·0402	0·0277	0·0683	0·0244	0·0507	0·0716
Lactate dehydrogenase, μ mole for mazan/g wet wt/hr	0·76	0·65	0·47	0·58	0·59	1·72

anaerobic bivalves where succinate is the end product of glucose degradation[22,23]. Glycolysis is diverted at PEP or pyruvate stage, in these animals forming oxaloacetate or malate respectively which ultimately form succinate.

The advantage of this pathway[24] is that it allows the reoxidation of $NADH_2$ produced in glycolysis without involving the formation of lactate. Of the two molecules of NAD reduced in glycolysis, one is regenerated in the conversion of OAA to malate and the other in fumarate reduction. The other advantage is that the reduction of fumarate to succinate by $NADH_2$, catalysed by the mitochondrial electron transport system, generates energy in the form of ATP[25].

The non-availability of oxygen, the increased glycolytic rate, the significant decrease in glycogen level without its concomitant appearance as lactic acid and the decreased rate of oxidative metabolism are indicative of an efficient metabolic diversion during aestivation in *P. globosa*. Probably the diversion occurs at PEP, since low *p*H and increased ATP and Ca^{2+} which prevail during aestivation are known to inhibit pyruvate kinase[26]. The second molecule of PEP which forms alanine[27] in bivalves may form either glutamate or aspartate through transmination, since the levels of these two amino acids increase multifold, whereas alanine is totally depleted during aestivation. Though succinate is the end product of glycogen metabolism in many bivalves and parasitic helminths, succinyl CoA also is formed in *Dicrocoelium*[28]. In *P. globosa*, it appears that the Krebs' cycle is reversed as far as succinyl CoA, which may be utilized to synthesize phosphobilinogen, a precursor of porphyrin biosynthesis[8]. Gastrohaematin, an iron porphyrin, with absorption spectrum similar to that of cytochrome b both in the oxidised and reduced states, was known to accumulate in the stomach of aestivated snail. The origin of gastrohaematin was traced to the disruption of mitochondria in the tissues. The similarity in the absorption spectrum of gastrohaematin and cytochrome b suggests that cytochrome b has moved out of the mitochondria and mobilized to stomach as gastrohaematin, indicating the disruption of an intact electron transport system. How specifically one component from an intact biostructure is removed is difficult to explain at this stage. Alternatively, it is possible that some mitochondria undergo lysis and the cytochrome pool is disintegrated and then synthesized into one component having a similar absorption spectrum as cytochrome b (Fig. 5). In this connection, succinyl CoA is useful to form δ-aminolevinulate, a precursor of porphyrin biosynthesis. Further, it was reported that the amount of accumulated gastrohaematin during aestivation is 8 times that in starvation[29]. Since non-availability of oxygen is the major factor that differentiates the two metabolic states, the increased accumulation of gastrohaematin during aestivation may be attributed to the reduced prominence of mitochondria and its retention of cytochrome b. Incidentally, it is interesting to note that the level of glycine used to form δ-aminolevinulate increases during aestivation.

Krebs' cycle — The reports on Krebs' cycle enzyme activities in *P. globosa* are scanty; decreased activity

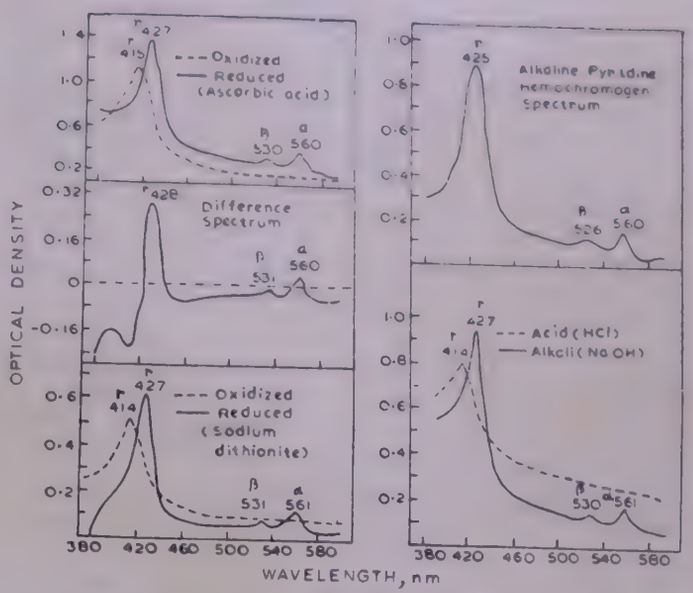


Fig. 5 — Difference spectrum, and absorption spectra with different oxidising and reducing agents of gastrohaematin [Note the occurrence of a single band (Soret band) in oxidised state and the appearance of α and β bands and a sharper soret (γ) band in reduced state]

is reported during aestivation. The decrease in activity in the case of succinate dehydrogenase[30] was supposed to be due to the decrease in enzyme-substrate affinity and the mitochondrial content[31].

Pyruvate and acetyl CoA are also formed from proteolysis, amino acid and fatty acid oxidation, since the contents of proteins and fats were reported to decrease during aestivation[31,32]. These might be used to detoxify the ammonia formed in amino acid and nucleotide metabolism by forming glutamate in the α-ketoglutarate step. The study of glutamate dehydrogenase with and without the coenzyme showed that the activity is more when optimal concentrations of NAD are provided, suggesting that *in vivo* the enzyme activity is poised towards the reductive amination of α-ketoglutarate. Further, it was reported that reduced NAD inhibits the α-ketodehydrogenase complex[33] and the reducing equivalents produced in the dehydrogenation of isocitrate might have imposed a premium on the oxidation of α-ketoglutarate.

Accumulation of haemoproteins during aestivation — The stomach of aestivating *P. globosa* was found to be filled with a thick, bright red, viscous fluid and preliminary analysis indicated the presence of a heme pigment in this fluid[29]. Spectral absorption analysis of this fluid showed bands characteristic of porphyrins α, β and soret (γ) bands in the reduced state, but only the soret band in the oxidised state (Fig. 5). A soret band at 400 nm is characteristic of the tetrapyrrole nucleus, porphin, of which all porphyrins and hence the hemes are derivatives. The appearance of a strong α-band and a weak β-band on treatment with reducing agents like sodium dithionite and ascorbic acid (Fig. 5) indicates that the porphyrin in the gastric fluid of *P. globosa* is in the form of a complex with a metal ion, capable of undergoing oxidation and reduction. Further, the appearance of α- and β-bands on reduction with sodium dithionite and

ascorbic acid indicates that the pigment in the gut fluid is in the oxidised state. An "intrinsic cytosomal electron acceptor" has been shown to be present in the nerve cells of pelecypods and *Lymnaea stagnalis* that is capable of 'anoxic endogenous oxidation'[34-37]. The mechanism of 'anoxic endogenous oxidation' involves the function of normal metabolic pathways maintaining the oxidative phosphorylation, with the exception that the electron transport taking place normally from $NADH_2$ up to O_2 is realized only to the redox potential of the cytochromes or lipochrome pigment. The redox potential of the pigment amounts to about E_{cal}=100-150, i.e. E_h=350-400. This is lower than that of O_2 (E_h=820 mV); nevertheless, it is even higher than that of cytochrome a. By this 'anoxic endogenous oxidation' 56-57% of the total energy is realized for the same amount of substrate used up. Gastrohaematin was supposed to originate in the hepatopancreatic cytochromes. The function of the oxidation-reduction system during aestivation is not known.

Proteins and amino acids — The protein level drops in the snail tissues on aestivation. The total protein content decreases by 12.5, 40 and 30%, sucrose soluble proteins by 4.29, 37.03 and 20.97% and sucrose insoluble proteins by 21.02, 43.02 and 39.3% in foot, mantle and hepatopancreas respectively in the aestivated *P. globosa*, indicating that both the structural and soluble proteins undergo disintegration in the mantle and hepatopancreas, whereas in foot, the soluble protein fraction is degraded to a lesser extent. Though mantle had more protein degradation than the other tissues, the free amino acid level is relatively low; suggestive of relatively greater amino acid utilization in mantle.

In the aestivated snail, the total free amino acid levels showed 4.5, 3·7. 15.71 and 15.24% increase in

TABLE 5 — ALCOHOL SOLUBLE FREE AMINO ACID CONTENTS (μ MOLE AMINO ACID/G WET WT) IN SELECTED TISSUES OF ACTIVE AND AESTIVATED *P. globosa*

Amino acid	Active			Aestivated		
	Foot	Mantle	Hepatopancreas	Foot	Mantle	Hepatopancreas
Glycine, serine and arginine	38·9	38·2	63·3	85·1	68·4	46·2
Alanine	58·2	32·6	16·6	3·2	2·5	—
Cysteine, cystine	28·0	46·5	31·1	99·6	28·0	20·4
Threonine	2·4	—	—	19·8	9·0	6·2
Aspartic acid	7·1	8·0	—	6·2	11·0	5·6
Glutamic acid	57·8	31·4	35·1	228·0	50·4	49·8
Lysine	112·7	45·5	32·8	21·6	51·3	38·2
Histidine	76·5	55·0	26·5	73·6	46·5	—
Leucine and isoleucine	10·4	8·0	—	25·0	10·4	12·9
Tyrosine	121·1	65·6	41·7	265·5	70·9	68·4
Valine, phenylalanine and methionine	4·7	4·0	—	20·0	6·0	10·0

TABLE 6 — CHANGES IN THE LEVELS OF AMINO TRANSFERASES IN SELECTED TISSUES OF ACTIVE AND AESTIVATED *P. globosa*

State of the animal	Foot[7]			Mantle[7]			Hepatopancreas[7]			Nervous tissues[17]		
	AAT	AlAT	TAT	AAT	AlAT	TAT	AAT	AlAT	TAT	AAT	AlAT	TAT
Active	7·5	25·2	0·71	2·8	6·5	0·77	3·1	2·5	1·4	1·87	1·75	0·016
Aestivated	6·2	3·0	3·6	1·8	3·2	1·7	1·2	1·5	2·1	1·17	1·21	0·0055
Incidence of change on aestivation, %	−17·3	−42·3	+441	−34·5	−50·4	+53·6	−61·3	−40·0	+58·7	—37	—31	—67

foot, mantle, hepatopancreas and body fluids respectively (Table 5). A prominent observation from the chromatographic analysis of free amino acid is the consistent increase in glycine complex, glutamate, lysine, histidine and tyrosine (Table 5). The increased glycine and glutamic acid contents may contribute to uric acid biosynthesis in the snail. The basic amino acids might serve to maintain the acid-base balance to facilitate normal functioning of the enzymes. The elevated tyrosine levels might be due to ths decreased activity of enzymes associated with melanin pigment formation, since pigmentation of the snail decreases in aestivation.

Aminotransferases — AAT and AlAT decrease by approximately 50%, except in the foot in the aestivated snail (Table 6), indicating that the formation of glutamate through transaminations is reduced and probably glutamate formation is supplemented by glutamate dehydrogenase in the tissues. Two isozymes for AAT, cytosolic and mitochondrial, having *p*H optima at 9 and 7 respectively were reported. But in the aestivated snail tissues maximal activity appeared in the acid *p*H, also indicative of the tendency towards splitting of the consolidated enzyme complex in aestivation. Tyrosine aminotransferase (TAT), low in active snail tissues, increased multifold in aestivation, indicating a role in demelanisation, which results in loss of pigment.

Glutamine synthetase — Glutamic acid was known to inhibit the electrical and other enzyme activities. Though it buffers ammonia toxicity in the aestivated snail, its level should be effectively controlled lest it should cause total cessation of activity. Of the possibilities, conversion of glutamate to glutamine which contributes to N_3 and N_9 of uric acid molecule, appears to be preferred and in this connection glutamine synthetase plays a pivotal role in the regulation of ammonia toxicity.

The activity of glutamine synthetase is limited only to hepatopancreas, suggesting that the synthesis of glutamine forms the bottleneck reaction in uric acid biosynthesis. Such control mechanisms limiting the entire pathway by some slow steps in the reaction sequences are not uncommon in animal biochemistry[38]. There is 100% increase in the glutamine synthetase activity level in the hepatopancreas of 1 month aestivated *P. globosa* and the activity is maintained at that level for 3 months of aestivation[38]. Though the cellular environment favours adenylylation or deactivation of the enzyme, the activity of the deadenylytating enzyme system is stepped up to cope with the demands of increased glutamine synthesis. Since in 6 months aestivated snail which relies less on proteins and amino acids for its energy as it is set with low energy demands, glutamine synthetase decreases and its activity is less than in active snail[39].

Nitrogen excretory metabolism — Nitrogen excretion in molluscs was studied extensively by Potts[43] and has been reviewed recently by Campbell and Bishop[41]. The nature of the predominant excretory product is still conjectural, since the reports for different gastropods are contradictory. But it is generally accepted that from primitive *Fissurella* to the modern prosobranch, *Thais lamellosa*, and the pulmonates, *Planorbis* and *Lymnaea*, there is a tendency to store uric acid in the tissues and that uricotelism is a characteristic of gastropods, in general, and is not related to the type of environment in which the snail lives[42].

Table 7 — Ammonia Content in the Body Fluid and Selected Tisisues of Active, Aestivated and Revived *P. globosa*

[Values represent μmoles ammonia/g wet wt of tissue or ml of body fluid]

	Body fluid	Hepato-pancreas	Mantle	Foot	Ambient medium
Active	2·14	67·65	65·91	38·75	—
Aestivated					
15 days	1·20	59·30	38·31	33·09	—
45 days	1·07	74·48	40·97	31·33	—
90 days	0·63	56·02	47·60	37·41	—
Revived					
1 day	0·88	69·41	38·66	28·99	1·49
6 days	1·12	49·10	26·35	28·99	3·16
12 days	0·86	48·13	28·99	19·34	7·03

Table 8 — Urea Content in the Body Fluid and Selected Tissues of Active, Aestivated and Revived *P. globosa*

[Values represent μmoles ammonia formed/g wet wt tissue or ml of body fluid]

	Body fluid	Hepato-pancreas	Mantle	Foot	Ambient Medium
Active	0·84	25·45	27·76	8·09	—
Aestivated					
15 days	0·07	6·45	7·23	5·06	—
45 days	0·05	11·24	7·21	4·7	—
90 days	0·09	8·17	5·42	BLD	—
Revived					
1 day	1·04	50·21	50·28	27·11	21·71
6 days	0·49	86·72	80·45	30·75	70·31
12 days	0·83	97·48	101·83	7·03	112·28

(a) *Ammonia* — There is 61% decrease in ammonia content in the mantle tissue of aestivated snail and the change in the other two tissues is not significant (Table 7). The loss of ammonia in the mantle may be attributed to volatilization[43]. But survival of *P. virens* in plastimold for several months unlike in its American counterpart, *Helix pomatia*, shows that this external excretion of ammonia is not absolute to the survival of the snail. The relatively insignificant change in ammonia level in other tissues speaks of an efficient mechanism of detoxification during this torpid state.

(b) *Urea* — An acute decrease, 89.29%, for body fluid, 67.4% for hepatopancreas and 84.47% for

mantle of urea in aestivated snail has been reported (Table 8). It is below the level of detection in the foot of aestivated snail.

Krebs-Hensleit cycle — Though the existence of an active urea cycle is much debated in gastropods, complete complement of enzymes has been reported in the land snails, *Otala lactea* and *Helix pomatia*. But Bricteux-Gregoire and Florkin were unable to detect carbamyl phosphate synthetase and ornithine transcarbamylase in *Helix pomatia*. Further, the two rate limiting enzymes were below the level of detection in many of the molluscs studied. Arginase is present in many molluscs and its activity ranges from 2000 to 45,000 units. But in *P. globosa*, the activity levels of arginase are 0.1, 0.14, 0.078, 1.79/mg protein/hr and 0.17, 0.26, 0.05 and 2.4/mg protein/hr in hepatopancreas, mantle, foot and intestine respectively in active and aestivated snails, indicating that the activity levels of arginase are too low to support urea biosynthesis in the tissues. Campbell[41] contends that there are interesting biochemical differences in the disposal of nitrogenous wastes between the land snails of America, and the Indian amphibious snail, *Pila globosa*. The investigations referred to in the succeeding sections show that stress is on uric acid metabolism during aestivation.

Table 9 — Uric Acid Content in the Body Fluid and Selected Tissues of Active, Aestivated and Revived *P. globosa*

[Values represent mg uric acid/g wet wt of tissue or ml of body fluid]

	Body fluid	Hepato-pancreas	Mantle	Foot	Ambient medium
Active	0·24	1·58	0·79	0·71	—
Aestivated					
15 days	0·18	2·63	3·13	2·16	—
45 days	0·75	11·13	11·97	5·25	—
90 days	1·15	10·22	10·74	8·49	—
Revived					
1 day	0·42	20·87	23·4	11·13	—
6 days	0·25	22·85	32·35	6·26	—
12 days	0·21	23·7	47·3	4·52	—

Table 10 — Xanthine Dehydrogenase Activity in Different Tissues of Active and Aestivated *P. globosa*

[Values represent μmole formazan formed/g wet wt tissue/hr]

	Active	Aestivated	% over active
Hepatopancreas	16·20	30·0	+85·21
Mantle	13·6	21·8	+60·3
Foot	6·43	12·56	+95·35
Intestine	8·53	12·96	+51·94
Heart	3·83	5·8	+52·63

Uric acid — A significant feature of the excretory metabolism of *P. globosa* during aestivation is the rate of increase in uric acid level in different tissues. The increase in uric acid level in the body fluid, mantle and hepatopancreas is highest during the first 45 days and thereafter the increase is at a lesser rate (Table 9). In fact, a significant decrease is observed in the hepatopancreas and mantle of 90 days aestivated snail when compared with 45 days one. This may be due to the protein catabolism prevailing in the initial stages of aestivation when the animal has access to the air entrapped in the mantle cavity for the oxidative deamination of amino acids and the oxidation of hypoxanthine or xanthine to uric acid. The decrease of uric acid in the mantle and hepatopancreas observed on day 90 of aestivation may be due to its mobilization to other tissues. The increase in uric acid level in the foot is slow and steady, presumably due to the predominance of carbohydrate metabolism, as foot is known to contain 80% of the total glycogen of the body and utilizes more glycogen than the rest of the organs.

Synthesis of Uric Acid during Aestivation

Needham[44] has pointed out that accumulation within a snail of less than 1 mg of uric acid could be due to nuclein catabolism. Uric acid values higher than 4 mg/g indicate synthesis of uric acid in these forms. It was shown that the synthesis of uric acid involves simple precursors, such as carbon dioxide,

Table 11 — Effects of Body Fluids on the Acetylcholinesterase (AChE) Activity in the Nervous Tissue Homogenates of Active and Aestivated *P. globosa*[17]

State of the animal	Controls	NBF	EBF	DNF	DEF	HNF	HEF
Active	7·1	7·3	6·1	5·3	6·1	8·8	8·5
Percent change over controls		+2	—14	—25	—14	+25	+18
Aestivated	4·7	6·8	4·8	4·3	3·7	6·2	6·3
% Change over controls		+46	+3	–7	–21	+34	+35

acetate, formate, glycine, aspartic and glutamic acid, as in other uricotelic vertebrates[45,46]. Uric acid biosynthesis involves the intermediary formation of hypoxanthine followed by its oxidation in the presence of the enzyme xanthine oxidase to uric acid.

Xanthine oxidase — Xanthine oxidase is present in the hepatopancreas of *Anodanta*[47], *Helix*[48] and *Pila*[49]. Ishida[50] found its major localization in the foot of *Meretrix*. Lal and Saxena[49] failed to detect the enzyme in the nephridium of *Pila globosa*. But xanthine oxidase activity is not limited to hepatopancreas alone and it is found in substantial quantities in the mantle, foot, intestine and heart (Table 11), suggesting that these tissues also have the potential to oxidise hypoxanthine to uric acid. In other tissues like penis and nephridium, uric acid accumulation was reported, but the enzyme activity was undetectable; the accumulation of uric acid in these tissues indicates that the uric acid synthesized actively in other tissues, viz. hepatopancreas and mantle, is transported to these tissues. The animal might have found these organs as convenient sites to pile up uric acid, as it probably goes beyond the capacity of the tiny nephridium to store all the uric acid synthesized in the body[51].

Excretory Metabolism during Revival from Aestivation

The nitrogenous excretory metabolism undergoes interesting changes during the revival of *Pila*. On the first day of revival, the animal showed a significant increase in urea and uric acid in all the tissues, indicating induction of rapid catabolism (Tables 8-10). Such boosting up of activity is also noted during arousal from hibernation in mammals[52,53]. But the sudden several-fold increase in the urea content on the first day of revival accompanied by a drastic fall in the uric acid content in the body fluid suggests a shift from uricotelism to ureotelism. In view of low activity of ornithine cycle enzymes and decrease in the uric acid levels of the body fluid, it appears that urea production at this stage may not be entirely through ureogenesis. Hence, urea production as a consequence of uricolysis seems probable.

During subsequent periods of revival, *P. globosa* shows a continuous decrease in ammonia levels in all the tissues and the body fluid, suggesting elimination of ammonia into the medium. This is further substantiated by the observed increase in ammonia content in the revival medium (Table 8).

The decrease in urea and uric acid levels in the body fluid and foot on subsequent days of revival with a simultaneous increase in urea and uric acid levels in the hepatopancreas and mantle may mean either loss of urea from the body fluid and foot or its transport from the foot to hepatopancreas and mantle via the body fluid. When *Bulimulus dealbatus* was revived from aestivation, rapid disappearance of the accumulated urea and uric acid was observed[54]. Urea was undetectable, whereas uric acid was always present. The uric acid content decreased by 24.8 and 79.39% in the kidney of 6 months aestivated *P. globosa* revived for 15 days and 27 days respectively[49]. On the basis of the detection of urea in increasing quantities in the revival medium, it might be suggested that the decrease in urea levels in the body fluids and foot might be due to excretion. Since excretion of uric acid from the foot to the medium cannot be suggested in a similar way, as uric acid was not detected in the revival medium, two alternatives are open for consideration. The first one is mobilization of uric acid from the foot and kidney to the mantle, since there is continued increase in the level of uric acid in this tissue even after revival. This is further substantiated by the continued decrease in uric acid level in the body fluids with prolonged revival periods. The second alternative is the degradation of uric acid and its subsequent excretion. Mobilization of uric acid in prosobranch, *Thais* has already been pointed out by Stickle[55]. Inspite of the phenomenon "enzymapheresis", wherein there is loss of enzymes of uricolysis with evolution, there will be interesting exceptions, because the conclusion is based on an examination of relatively few species and on the work prior to 1950 with relatively less sophisticated methods and instruments. Gostan[56] showed the existence of all uricotelic enzymes in the marine gastropod, *Nerita albicilla*. A related snail, *Nerita costata*, which lives in the upper littoral zone, possesses low level of uricase and no allontoinase, allontoicase or urease. Uricase and other uricotelic enzymes have been reported in the hepatopancreas of *P. globosa*[51]. It is clear from the above reports that the distribution of uricolytic enzymes follows no general pattern and it depends on the animal under investigation, as two closely related species under different environments possess contrasting enzyme activities.

With the reservation that the presence and activity of uricolytic enzymes in active, aestivated and revived *P. globosa* remain to be established, it may be assumed that the activity of uricolysis is localized mainly in hepatopancreas and mantle and uric acid from other tissues like foot, kidney, heart, stomach, penis, vegina, testis and uterus is mobilized to these tissues when the animal is revived; in these tissues it is broken down and excreted out as ammonia and urea. It is otherwise not possible to account for the large increase in urea level in all the tissues on revival in view of the low levels of ornithine cycle enzymes and the high levels of uric acid in mantle and hepatopancreas.

It appears that the nitrogenous waste product is so chosen as to be of advantage to the survival of the animal. The highly adaptive nature of the nitrogenous excretory pattern in gastropods has been emphasized by Sloan[57]. The two closely related fresh water prosobranchs, *Marissa* and *Pomacea*, differ in their mode of egg laying. *Marissa* lays eggs in the water, while *Pomacea* lays its eggs above the water level on the emergent vegetation. The developing *Pomacea* eggs accumulate uric acid and ammonia, while *Marissa* eggs accumulate and lose ammonia to the ambient medium, indicating the labile and adaptive nature of the nitrogenous excretory pattern in gastropods.

Uricolysis and urea excretion may be significant, because urea can be excreted more rapidly than uric acid owing to its smaller molecular size and greater solubility. Studies on the renal physiology of large pulmonates, *Achantina fulica* and *Strophocheilus*

oblongus, have shown that urea is rapidly cleared by kidney. From the free energy viewpoint, ammonia and urea would be the most efficient excretory products and uric acid, the least efficient one. It follows that the metabolic pattern and excretory products are well organized to suit the self withdrawn states of the animal during aestivation.

Regulation of Aestivation Metabolism

Many investigators attempted to isolate the active principle bringing about the fine control in the aestivation metabolism and there is much variance of opinion on this point. Danforth[60] has pointed out that in the regulation of the enzyme action in living systems, search for the single regulator of an important pathway is often in vain and the rate of flow over a multi-enzyme pathway may be controlled by the cooperative action of more than one enzyme and perhaps multiple activators and inhibitors, the importance of each varying with the physiological circumstances.

Meenakshi reported that aestivation in *P. globosa* is under hormonal control[43]. The rise in the calcium and magnesium levels in the aestivated snails appears to be under the influence of a non-cholesterol type of steroid hormone produced in the cerebral ganglia. When aqueous, ether and alcohol extracts of the cerebral ganglia of aestivating *Pila* are injected into active *Pila*, the calcium and magnesium levels rise and the respiration is lowered. The neuroendocrine control of aestivation metabolism is receiving increasing attention and many workers are inducing aestivation effects in active snails by injecting the extracts of cerebral ganglia of aestivated snails. If the active principles are synthesized in cerebral ganglion, they should be released to the body fluids. The body fluids elicited a similar response (Table 11) and on analysis, the active principle was found to be dialysable and thermostable and to have a low molecular weight; it is probably of the nature of an amino acid. The effects of amino acids on the nervous and enzyme systems were studied extensively[59,60]. Among the amino acids, glutamic acid was found to have pronounced inhibitory effect on the nervous system and different enzyme systems.

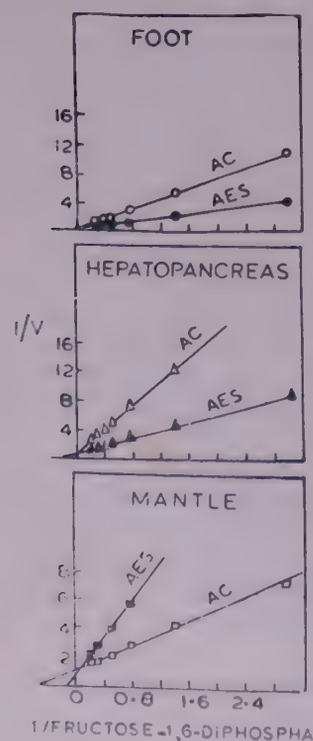


Fig. 6 — Double reciprocal plots for aldolase in different tissues of active and aestivated *Pila* [Ac, active, Aes, aestivated]

The responsiveness of a tissue depends on the energy availability and cellular oxidations, in addition to irritability. The energy source could be the anaerobic or aerobic segments regulating metabolite oxidations. Increased aldolase levels, as reported earlier, suggest an elevated activity of the anaerobic segment of carbohydrate metabolism.

The substrate-velocity relationships for aldolase show a decrease in the value of K_m in the foot, hepatopancreas and mantle, indicating an increase in the ES affinity in all the tissues (Fig. 6). Though mantle has an increased efficiency of enzyme catalysis, the enzyme content is apparently less, as revealed by decreased value of V_{max}. The addition of glutamic acid increases aldolase activity in active snails and decreases the same in aestivated snails.

The decrease in SDH activity appears to be due to change in the enzyme content in the foot and hepatopancreas, since the value of K_m is unaltered in these tissues. Since the calcium content is known to increase in the visceral mass during aestivation, its effect was studied. Calcium inhibited SDH in all the tissues non-competitively; this could be reversed by the chelating agents, sodium citrate and EDTA.

General Conclusions

Aestivation in *P. globosa*, is associated with decrease in calcium content of the shell and operculum and increase in the calcium and magnesium levels in the body fluid[61]. The visceral mass shows increased calcium content. Meenakshi[23] reported that increased blood calcium helps in buffering the acid metabolites and magnesium serves as an anaesthetising agent. The metabolic fuels like protein are lost in all the tissues. George and Desai reported that the liver fat content falls during aestivation in *Pila globosa*[61]. Greater loss of sucrose insoluble proteins than sucrose soluble protein, suggests that the structural components of the cell are disintegrated. Decrease in the level of protein should result in an increased amino acid pool, but interestingly the levels of not all amino acids increase during aestivation. Glutamic acid, aspartic acid and glycine complex (making allowance for the amount utilized in uric acid biosynthesis) increase to a large extent. Tyrosine, cystine, leucine and valine increase in the foot, but in hepatopancreas and mantle, the increase is not significant. It appears that uric acid biosynthesis is active in hepatopancreas and mantle and hence one can observe a much greater increase in the level of uricogenic amino acids in mantle and hepatopancreas. The foot is probably less important in uric acid production, as is evidenced by the low level of uric acid and the slow increase in it observed during aestivation. Hence, an increase in the levels of all the amino acids is observed in the foot during aestivation.

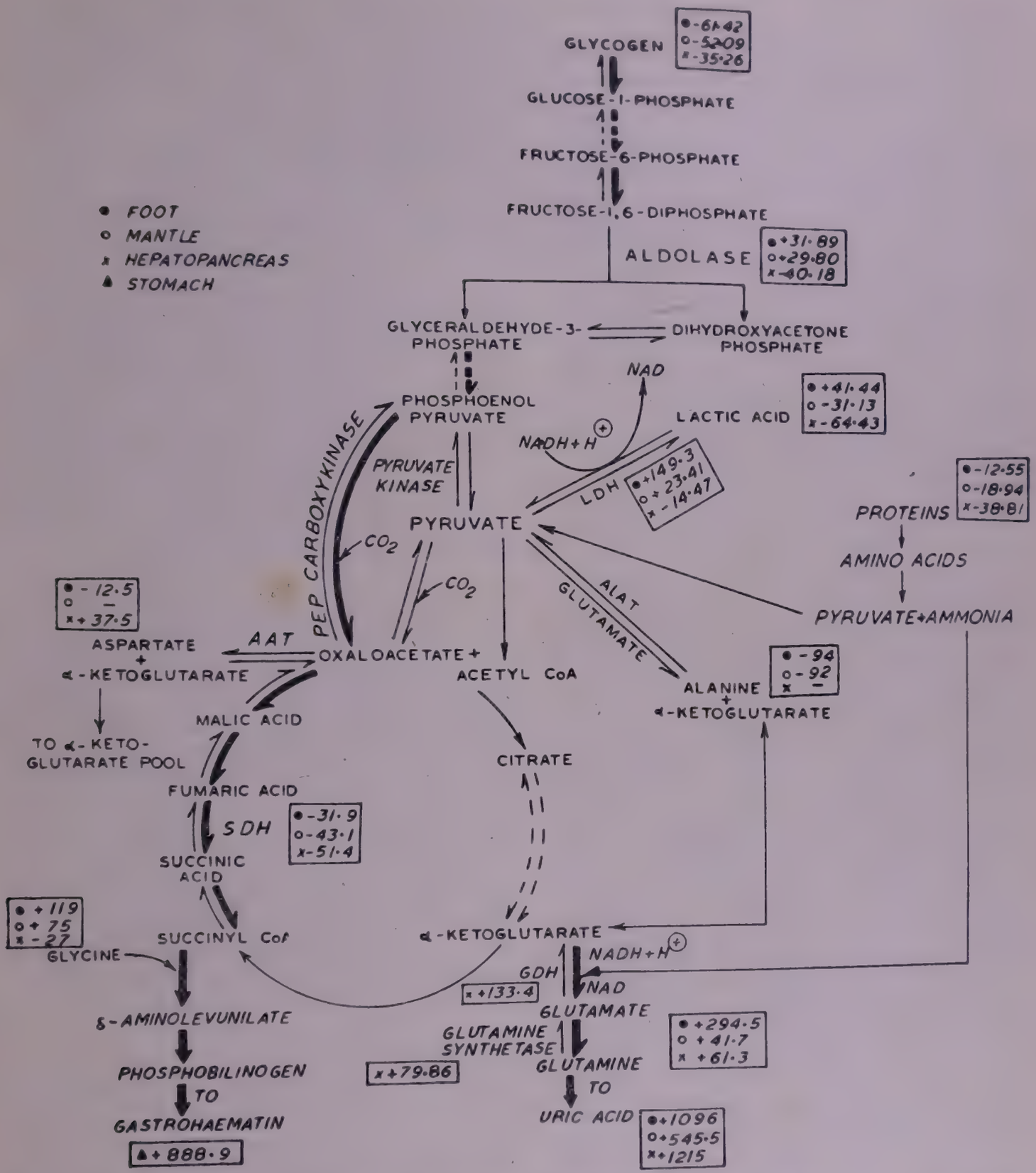


Fig. 7 — Schematic representation of the probable pathway of intermediary metabolism during aestivation in *Pila globosa* [The '+' or '—' signs in rectangular boxes indicate the increase or decrease respectively over their respective controls in active snails. The heavy lines indicate the direction in which stress is laid in the flux of metabolites]

Amino acid oxidases are active in molluscs axiomatically, resulting in the production of ammonia, which condenses with α-ketoglutarate to form glutamate. Increased glutamate dehydrogenase concurrs with the above assumption. Glutamic acid, by transamination with oxaloacetate, forms aspartic acid and α-ketoglutarate. The α-ketoglutarate formed in this reaction may be utilized to trap the ammoina. For

this mechanism to be viable, there should be continuous production of α-ketoglutarate and oxaloacetate.

Carbon dioxide fixation of either pyruvate or PEP by pyruvate carboxylase or PEP carboxykinase results in the production of oxaloacetate. Both the enzymes are reported to be very active in molluscs. Further increased glycolytic rate, decreased lactate production and lactate dehydrogenase activity and decreased oxidative metabolism indicate diversion of flux of metabolites at some stage in glycolysis. In the absence of previous reports on the relative activities of the two enzymes, it is difficult to assess at what stage glycolysis is diverted.

Whether the oxaloacetate formed is used only for transamination, resulting in the production of aspartate, or it undergoes further reactions, is difficult to answer at this stage. Studies on allied molluscs suggest that it may be converted to succinyl CoA. This assumption explains the regeneration of NAD in the presence of low lactate dehydrogenase activity and reduced oxygen consumption. The succinyl CoA and glycine may form δ-aminolevinulate, which may be used for haematin synthesis. The increased accumulation of gastrohaematin in the gut is evidence for this contention. Again, how far the synthesis, occurs in the tissues and mobilized to the gut is an important question to be answered.

The sources of α-ketoglutarate may be the pyruvate fed to the Krebs' cycle by glycolysis or by deamination of amino acids. Fatty acid oxidation results in acetyl CoA and the level of fatty acids is known to fall in the hapatopancreas during aestivation. The amination of α-ketoglutarate appears to be preferred than its oxidation by α-ketoglutarate dehydrogenase. This may be the possible mechanism by which the levels of glutamic acid and aspartic acid alone increase, while a similar increase could not be seen in the levels of the other amino acids, as expected by proteolysis.

Glutamic acid is known to inhibit the electrical activity and other enzyme activities. Hence, it should not accumulate in the tissues lest it should cause total cessation of activity. Two possible routes could be visualized for the metabolism of glutamic acid in tissues. It can be converted to urea via aspartic acid through the ornithine cycle, or to uric acid. The former possibility is excluded in view of the low urea content in aestivated snail tissues. The other possibility that glutamic acid is utilized in the biosynthesis of uric acid seems to be more probable in view of the increasing quantities of this purine in the tissues of the aestivating *P. globosa*. This requires the enzyme glutamine synthetase which is present only in hepatopancreas, suggesting that the synthesis of glutamine forms the bottleneck reaction in uric acid biosynthesis. In the absence of any report on the distribution of the enzymes involved in purine biosynthesis, it is not possible to assess how far the synthesis of uric acid occurs in the tissues through xanthine oxidase which is present in most of the tissues.

It is astonishing to note how the snail prefers to produce uric acid, which is a costly waste product requiring much of ATP bond energy at a time when the demand for energy is very high. It is equally surprising for the snail to maintain a high ATP level inspite of the accumulation of high amounts of uric acid. Cessation of locomotory, reproductive and other physiological activities might help to conserve much energy. The low ATPase activity is indicative of the slow utilization of ATP. The ATP saved could be helpful in uric acid synthesis.

The revival of the snail is associated with the restoration of ATPase activity and synthesis of gastrohaematin. The uric acid content in the foot, kidney and probably other tissues decreases, while it increases in hepatopancreas and mantle. Uric acid did not make its appearance in the ambient medium, which shows only increasing quantities of ammonia and urea. It appears that uric acid is broken down and excreted. With the restoration of oxidative metabolism, $NADH_2$ can be oxidised through electron transport with its concomitant inhibitive action on α-ketodehydrogenase complex. α-Ketoglutarate can now be oxidised without being reductively aminated by glutamate dehydrogenase. The ammonia formed in the body can be excreted as such without being converted to uric acid. Thus, *P. globosa* represents an interesting case of suspended animation and coming back to normal life when put in water; in both cases the biochemical changes are so regulated as to exploit the imposed environmental stress.

Summary

The metabolic alterations in the tissues of *Pila globosa* during aestivation are discussed. While the citric acid cycle oxidations get diminished, there is increase in the glycolytic enzyme activities. The glycogen levels decrease in all the tissues, while the lactate content increases in the foot and decreases in the mantle and the hepatopancreas. Decreased keto acid oxidations and elevated protease activity and amino acid levels are indicative of the disturbance in the carbohydrate and protein metabolisms; the low aminotransferase activity is in agreement with this observation. Ammonia toxicity is averted by elevated activities of glutamate dehydrogenase and glutamine synthetase. The urea content decreased and the uric acid content increased in the tissues and the body fluid. The xanthine oxidase activity increases in the hepatopancreas, mantle, foot, heart and intestine. Electrical activity and acetylcholinesterase activity show correspondence with the overall activity.

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Abbreviations used: NAD, Nicotinamide adenine dinucleotide; $NADH_2$, reduced nicotinamide adenine dinucleotide; PEP, phosphoenol pyruvate; ATP, adenosine triphosphate; SDH, succinate dehydrogenase (Succinate:acceptor oxidoreductase; EC 1.2.99.1); AAT, aspartate aminotransferase (1-aspartate-2-oxoglutarate aminotransferase EC 2.6.1.1);

BLD, below the level of detection; AlAT, alanine amino transfersferase (1-alanine-2-oxoglutarate amino transferase EC 2.6.1.2); K_m, Michaelis constant; and V_{max}, maximum velocity.

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Diffusive Resistance Measurements : Theory and Application*

M. V. K. SIVAKUMAR † & R. E. CARLSON
Iowa State University, Ames, Iowa, USA

ENVIRONMENTAL water deficits have long been recognized as the chief limiting factors for crop production in many areas of the world. For example, an estimated 71% of the precipitation received by the United States disappears through evapotranspiration from non-irrigated pastures, meadows, cultivated fields, forests, and uneconomic stands of plants[1]. A part of the billions of gallons that escape each year through evapotranspiration escapes directly from the soil, but much, perhaps most, is transpired through leaf stomata or pores no larger than 35 by 15 μm (ref.2). In this context, the study of stomata and their effect on diffusion or transpiration of water becomes extremely important.

A better insight into the crop growth processes has been made possible by the recent development of simulation models of plant growth. Microclimate models play an extremely important role in such simulation work. Monteith[3] pointed out that the main limitation of microclimatic models is the ignorance regarding spatial changes of the epidermal resistance of leaves within plant canopies.

An attempt is made here to present the concept and the underlying theory of diffusive resistance. A few diffusive resistance experiments are discussed for illustration; it is not our purpose to present an extensive review on diffusive resistance measurements.

Theory of Diffusion

In the presence of a gradient of concentration of water vapour X or of carbon dioxide in air, molecular agitation is responsible for transfer of mass via diffusion[3]. The transfer of molecules, expressed as mass flux per unit area, E, is proportional to the concentration gradient.

$$E = -D\frac{\partial X}{\partial z} \qquad \ldots(1)$$

where D is the molecular diffusion coefficient for water vapour, and z is the linear distance directed away from the surface under consideration. Values of D at different temperatures can be calculated from the Chapman-Eskog kinetic theory of gases[4].

In a one-dimensional case, flux, though a variable depending on D, z_1 and z_2, can be treated as constant in the direction specified by the coordinate z at right angles to the surface.

$$E = \frac{X(z_1) - X(z_2)}{\int_{z_1}^{z_2} \frac{dz}{D}} \qquad \ldots(2)$$

Eq.(2) is analogous to Ohm's law, where

$$\text{Current} = \frac{\text{Potential difference}}{\text{Resistance}} \qquad \ldots(3)$$

Diffusion coefficients have dimensions of (length)^2 $\times$ (time)$^{-1}$, so that the corresponding resistances have dimensions of (time) $\times$ (length)$^{-1}$. A system in which the rates of diffusion are governed purely by molecular processes, the coefficients are usually assumed to be independent of z, so that $\int_{z_1}^{z_2} dz/D$ is $(z_2 - z_1)/D$, or diffusion path length/diffusion coefficient. Hence, Eq. (2) becomes,

$$E = \frac{D\,X(z_1) - X(z_2)}{z_2 - z_1} \qquad \ldots(4)$$

This is the well known Fick's law of diffusion, where

$$\text{Flux} = \text{Diffusion coefficient} \times \text{Gradient} \qquad \ldots(5)$$

Resistance to Flow through a Plant

Van den Honert[5] concluded that the major resistance to water flow in the plant is in the gaseous phase above the transpiring surface. Levitt[6] argued, from a consideration of vapour pressures, that the major resistance to flow through plants is in the liquid phase and not in the gaseous phase. Later, several workers[7-10] supported Van den Honert's view.

By treating water flow as analogous to energy flow, Boyer[11] calculated that the resistances in the sunflower plant for root, stem and leaves are in the ratio 2:1:1. Kramer[12] suggested the existence of significant resistances to water flow within the leaves.

Resistance in a Leaf

In the analysis of evapotranspiration from a cropped surface, climatologists are concerned with stomata and diffusion of water vapour through them. When leaves transpire, water evaporates from cell walls and escapes into the atmosphere by diffusing into substomatal cavities, through stomatal pores, and finally through the leaf boundry layer into the free atmosphere. During photosynthesis, the molecules of CO_2 follow a similar diffusion path, but in the opposite direction. The resistance offered by the boundary layer to the diffusion of a gas depends on leaf dimensions and on wind speed, whereas the resistance of stomatal pores depends on geometry, size and spacing of pores, and on associated anatomical features.

Considering the resistance to water vapour diffusion in and over a leaf, Slatyer[13] explained that the diffusive resistance of water vapour for a leaf, R_l, is formed by a normally high cuticular resistance in parallel to the resistance in the stomatal cavity and the substomatal pore (end effects included) with the effective

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†Present address : International Crops Research Institute for the Semi-arid Tropics (ICRISAT) 1-11--256 Begumpet, Hyderabad 500 016.

boundary layer resistance, r_a, in series with the resultant of others (Fig. 1). For typical broad-leaved plants, and assuming a smooth flow of air across the leaf, r_a is generally found to vary with leaf width and wind speed. For leaves of about 10 cm width, typical values of r_a range from about 1·5 sec/cm at a wind speed of 0·1 m/sec to 0·15 sec/cm at 10 m/sec. Comparable r_a figures for a 1 cm wide grass leaf can be expected to be 0·5 and 0·05 sec/cm, respectively[14]. Estimates of cuticular resistance (r_c) range from <10 sec/cm to >100 sec/cm (ref. 15). For a number of crop plants, however, values of r_c range between 10 and 40 sec/cm. Monteith[3] mentioned that r_c values range from 20–60 sec/cm in mesophytes to 40–400 sec/cm in xerophytes.

By comparison, typical, open stomata (r_s) values range from <1 to >10 sec/cm. With wheat, for example, r_s values of 0·25–2·4 sec/cm have been obtained[16–18]. Cuticular resistances are usually so much larger than stomatal resistances that their role in water vapour and CO_2 transfer can generally be ignored[3].

Resistance Calculations

Monteith[3] gave a detailed discussion for the calculation of stomatal diffusive resistance.

According to the theory of diffusion of a gas in three dimensions through a circular hole with diameter d in a plate whose thickness is d, the resistance of each side of a circular hole is

$$r_h = \frac{\pi d}{8D}$$

where D is the diffusion coefficient of the gas. The resistance of a laminar boundary layer of thickness t is

$$r_a = t/D$$

and the diffusive resistance within a uniform pore is

$$r_p = l/D$$

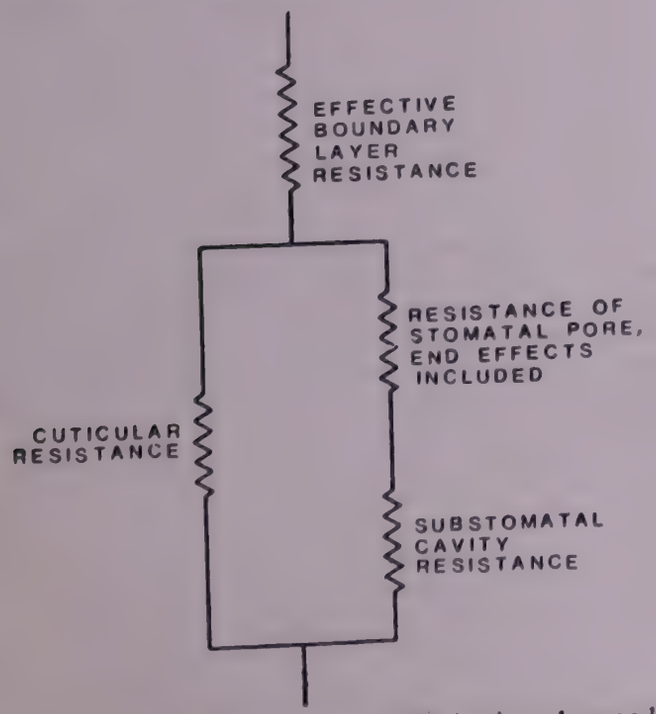

Fig. 1 — Resistance to water vapour diffusion in and over a leaf

where l is the pore length. The total resistance of a pore, r_t, is found by adding r_p to the resistance r_h at either end of the pore, i.e. $r_t = r_p + 2r_h$. For leaf stomata, r_h is often smaller than r_p ; r_h is referred to as an "end correction".

For a real pore and substomatal cavity, the end correction for a circular pore is assumed to be $2r_h = d/4D$, where d is a representative diameter, but it would be incorrect to apply a conventional end correction to the inner end of the pore. For many leaves, $r_t = r_p + r_h$ is a better estimate of the resistance of a single pore than is $r_t = r_p + 2r_h$.

If there are n pores per unit of leaf area, the resistance of a set of pores, r_s, can be derived from the resistance of individual pores (r_t). The transpiration rate can be written as $E = \partial X/r_s$, where X is the water vapour concentration. But r_s has to contend with the resistance offered across the area occupied by n stomata. Because the area of a single stoma is $\pi\ (d^2/4)$ (assuming circular geometry), the total area across n stomata is $n\pi\ (d^2/4)$.

Hence,

$$E = \frac{\partial X}{r_s} = \frac{n\pi\ (d^2/4)\ \partial X}{r_t}$$

from which it follows that

$$r_s = \frac{r_t}{n\ d^2/4}$$

But, previously, r_t was defined as

$$r_t = r_p + r_h$$

So,

$$r_s = \frac{4(l + \pi d/8)}{\pi\ n d^2 D} \qquad ...(6)$$

The Instrument

One of the most common diffusive resistance porometers in use in the United States is the one designed by Van Bavel *et al.*[19] and later modified by Kanemasu *et al.*[20,21]. This instrument is battery operated for portability and use in field operations as well as in confined spaces, such as controlled environmental chambers.

The diffusive resistance porometer consists of a moisture sensor, a resistance meter, and a drying tube assembly. A calibrated thermistor is included in the assembly for the measurement of temperature of air inside the porometer cup. The resistance meter can be operated in two humidity ranges. Humidity 1 and humidity 2 ranges are used for leaves with low and high diffusive resistances, respectively. The meter is adjusted with the knob labelled "cal" to give a full-scale reading with the function switch at the "end" position. The drying tube assembly includes silica gel, a dust filter, an air bulb pump and a hose.

Theory of the instrument — For direct measurement of the epidermal resistance to diffusion of water vapour, the closed diffusion porometer is the most promising instrument. The vapour flux of water vapour from mesophyll cell walls through the epidermis of the leaf is detected directly. Stigter *et al.*[22] gave a detailed account of the theory of the instrument.

The diffusion porometer consists of a small cup containing an electrical humidity detector. The device is placed onto the leaf; the initially low absolute cup humidity increases as water vapour diffuses into the chamber from the leaf. The transpiration rate is determined by the leaf resistance and also by a new diffusion resistance of the boundary layer to the presence of the porometer. This rate also is determined by a new leaf temperature, which has to be constant over a measuring period, and the (changing) absolute humidity in the cup. The rate of absolute humidity itself is determined by the transpiration rate.

Ideally, the rate change is indicated directly by the rate of decrease of electrical resistance of the humidity sensor. The time needed for a fixed decrease of sensor electrical resistance is now taken as a measure of the diffusive resistance. Cup air temperature also must be measured because of the temperature dependence of the diffusion process. After each resistance measurement, the cup air is dried to the original starting point.

Taking our analogy from Ohm's law (Eq. 3), evaporation from a saturated surface at constant temperature to a half-infinite space of constant vapour concentration, X_p, is described as:

$$E = \frac{X_l - X_p}{r_2 + r_p} \qquad ...(7)$$

where E is the vapour flux/unit area/unit time; X_l, absolute humidity at the evaporating surface of a leaf; X_p, absolute humidity within the porometer; and r_l and r_p diffusive resistance for water vapour of the leaf and porometer, respectively. When the half-infinite space is replaced by the humidity sensor cup, X_p is a function of time. The change in concentration is given by

$$\frac{dX_p(t)}{dt} = E(t)\frac{A}{v} \qquad ...(8)$$

where A is the surface area of the porometer entrance; c, air volume of the porometer; and v, cup volume of the porometer.

$$\frac{dX_p(t)}{dt} = \frac{X_l - X_p(t)}{r_l + r_p}\frac{A}{v} \qquad ...(9)$$

Let $\dfrac{A}{v((r_l + r_p)} = k$, a constant.

Now $\dfrac{dX_p(t)}{dt} = k[X_l - X_p(t)]$

and

$$\frac{dX_p(t)}{k[X_l - X_p(t)]} = dt$$

Integrating between two transient times $t = t_1$ to $t = t_2$ (representing moments of successive indication of two fixed electrical resistance values of the humidity sensor), we obtain for measured transient time,

$$t_2 - t_1 = \triangle t = \frac{v(r_l + r_p)}{A} \ln \frac{X_l - X_p(t_1)}{X_l - X_p(t_2)}$$

$$\triangle t = c(r_l + r_p) \qquad ...(10)$$

where

$$c = \frac{v}{A} \ln \frac{X_l - X_p(t_1)}{x_l - X_p(t_2)}$$

The instrument is calibrated by using an appropriate resistance plate with drilled holes to simulate leaf resistance. The resistance values can be calculated using Eq. (6). The average lapse time, $\triangle t$, is recorded for each resistance value and is plotted against resistance values.

The slope c of the curve is obtained from Eq. (10). Extrapolation to $\triangle t = 0$ gives $r_l = -r_p$. The measured $\triangle t$ values in the field are now directly related to leaf resistance via Eq. (10).

In the field, the meter is first checked by adjusting it to full scale reading with the "cal" knob. The sensor is cycled through dry to moist cycles before the first reading is taken. A leaf optimally oriented to the sun is usually selected, and the sensor cup is attached to the leaf. The time ($\triangle t$), for needle movements between the same points that were used in calibration is recorded. The diffusive resistance could be calculated by using the calibration curve. During field operation, care must be taken to see that the sensor cup is shaded from direct sunlight. Also, the sensor should be stored in a desiccator when not in use.

Application of Diffusive Resistance Measurements

Kanemasu and Tanner[20] obtained a very good correlation between stomatal conductance and turgor potential, where conductance is the reciprocal of resistance. Because turgor potential is influenced profoundly by the transpiration rate, there seems to be a direct coupling between stomatal conductance and transpiration.

Studies conducted at the Western Iowa Experimental Farm (Sivakumar, M.V.K., unpublished data) indicated a close relationship between the relative growth rate and the stomatal conductance ($r^2 = 0{\cdot}83$). These data suggest that the growth of the plant is regulated through the stomatal apparatus, whatever the mechanism that determines stomatal conductance.

The increase in stomatal resistance during a period of moisture stress increases the diffusive resistance of both water vapour and CO_2; therefore, if the CO_2 supply to photosynthetic sites is limiting, we would expect a decrease in both photosynthesis and transpiration. Kanemasu and Tanner[20] observed a reduction in the net assimilation rate that occurred when stomatal resistance and leaf water potentials were changing rapidly. This was attributed to (i) increased

respiration rate because of the high leaf and root temperatures caused by a decrease in transpiration and a higher heat flux to soil, and (ii) decreased photosynthesis owing to a decrease in CO_2 supply and hydration effects on biochemical processes.

Turner[23] observed a mid-day increase in leaf diffusive resistance with depth in the crop canopies of three species: maize, sorghum and tobacco. At noon, the upper leaves were fully illuminated, but the illumination declined rapidly within the canopy, resulting in mean values of less than 3000 ft-c in the lower leaves of all three species. Turner[23] concluded that, in well-watered crops, light is a primary determinant of stomatal resistance, but, in situations akin to that of tobacco in which a large proportion of leaf area has non-functional stomata or where a large proportion of the crop is senescing, consideration must be given to the inability of stomata to respond to light.

From a study in which illumination remained constant throughout the day, Heichel[24] concluded that the changes and rhythms in leaf diffusive resistance were random on leaves attached to plants in a constant environment.

As water deficit develops in the leaves and as the leaf water potential decreases, the stomatal resistance increases. Clark and Hiler[25] were of the opinion that leaf diffusive resistance became much more responsive in the later stage of growth when leaf water potential was least responsive. Recently, the concept of stomatal diffusive resistance has been extended to pollution studies. The stomatal resistance of tobacco plants exposed to ozone (O_3) showed a considerable increase over those not exposed[26].

The use of the concept of stomatal diffusive resistance is indispensable in plant-water relations research. Recent developments in diffusion porometry, combined with the growing interest in plant response to atmospheric evaporative demand, are responsible for the increased activity in this field. The extension of diffusive resistance ideas into other fields seems imminent. According to Gardner[27], in evaluating the water factor in agroclimatology, the stomatal resistance seems to be the most useful single measurement.

Summary

The concept of diffusive resistance is of major importance in investigations concerning water vapour and carbon dioxide flux in plant canopies. An attempt has been made to provide a simple discussion of the theory of diffusive resistance leading to instrumentation and field application. The magnitude of different resistances to water transport has been described. Finally, through the discussion of a few field experiments, the growing need for detailed field measurements has been stressed.

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REVIEWS

ADVANCES IN INFRARED AND RAMAN SPECTROSCOPY, Vols. I, II & III, edited by R.J.H. Clark and R.E. Hester (Heydon and Son Ltd, London), Vol. I, 1975; Vol. II, 1976; Vol. III, 1977. Pp. Vol. I, xiii + 306; Vol. II, xv + 343; Vol. III, xv + 285. Price Vol. I, £ 15·75, Rs 242·00; Vol. II, £ 17·50, Rs 280; Vol. III, £ 17·50, Rs 280·00

This is the first time a series publication has appeared containing a set of uptodate review articles covering a wide range of topics in infrared and Raman spectroscopy, thus recognizing the close and complementary relationship between these two methods of study widely used by physicists, chemists and biologists. Each volume contains six critical reviews by experts on those aspects of infrared and Raman spectroscopy where much progress has been made in recent years. The major objective of the edition has been the integration of theory and practice.

Volume I starts with an article on digital methods of Raman spectroscopy by J. R. Downey and G. J. Janz. The use of computers in Raman spectroscopy and also the hardware and software accessories necessary for linking the spectrometers with computers for optimum use are reviewed. In Chapter 2 entitled Raman spectroscopy of proteins, G. Fruchour and J.L. Koenig have reviewed the conformation studies of polypeptide chain in proteins. Starting with an introduction to protein structure, the authors have discussed the theory and techniques of Raman spectroscopy and have given the current literature involving globular and fibrous proteins and structure-frequency correlations. T. G. Spiro and T.M. Lochr have reviewed the work on resonance Raman spectroscopy (RRS) of heme proteins and other biological systems. Starting with the theory of resonance enhancement, the authors discuss the use of RRS for the study of structural features of specific sites of activity in biological molecules. Chapter 4 contributed by R.J.H. Clark deals with RRS of inorganic molecules and ions. The RR spectra of structurally simple inorganic molecules which possess absorption bands in the visible region have been reviewed and the use of RRS for the detection of small amounts of atmospheric pollutants is indicated. In Chapter 5, N. Mohan, A. Muller and K. Nakamoto have reviewed the applications of the metal isotope effect to inorganic vibrational spectroscopy. The final chapter by D.S. Steele deals with absolute absorption intensities as measured in the gaseous phase.

The first chapter of Volume II, by J.K. Burdett, M. Poliakoff, J.J. Turner and H. Dubost, deals with vibrational energy levels in matrix isolated species. The techniques of trapping and then taking the infrared and Raman spectra of unstable species of metal carbonyls and the extraction of information regarding structure, vibrational relaxation and every transfer in matrix isolated molecules have been described. In Chapter 2, C.D. Flint reviews the vibrational fine structure of electronic spectra of transition metal coordination compounds and the direct observation of inactive infrared and Raman fundamentals. The many aspects of the development of analytical infrared spectrometers for applications in industrial and production units are reviewed by H.A. Willis in Chapter 3. In the next chapter, M. Bridoux and M. Delhaye have reviewed the development of time resolved and space resolved Raman spectroscopy for the study of fast chemical reactions in gaseous, liquid and solid phases, photochemical processes, transient species, electronically, vibrationally and rotationally excited states, phase transitions and defects in solids and for the analysis of heterogeneous samples. The application of this new technique for microanalysis and Raman microscopy is also indicated. Chapter 5 by J.P. Devlin deals with the advances made in our knowledge of structures of molten salts which have resulted from infrared and Raman spectroscopic studies and the available data on ionic vapours and molten salts are reviewed. The last chapter by D.E. Irish and M.H. Brooker contains a review of the work carried out since 1971 on the Raman and infrared spectra of electrolytes in aqueous, non-aqueous and mixed solvents. More than 650 references connected with the studies in this field have been cited.

In the first chapter of Volume III, W. Kiefer reviews the recent developments in instrumentation and techniques of laser Raman spectroscopy which permit the recording of Raman spectra of a great variety of compounds from deeply coloured and even black materials to highly fluorescent molecules. The important innovations are automation, the rotating sample techniques and difference Raman spectroscopy. In Chapter 2, N.W. Stone and G.W. Chantry describe the experimental techniques and computational problems of extracting maximum information in the far infrared region with the Fourier transform interferometer. Advances have been made in precision measurements of intensity and wave number of absorption bands of gases, monitoring of trace gases in the higher atmosphere and the time resolved spectrometry of transient plasmas. The third chapter by P. Gans deals with force constant calculations. He has specially dealt with the tactics employed for obtaining meaningful results from force constant calculations. In Chapter 4, I.W. Shepherd reviews the work on measurement of polarizations of Raman lines, with special reference to structure of synthetic and biological polymers. The fifth chapter by D.J. Gardiner concerns vibration spectra of non-aqueous solutions. The review consists of a survey of many solvent systems and of the molecules and ions which may be present therein and their characteristic spectra. The vibrational spectroscopic data relating to solution systems in more than 25 inorganic solvents and 10 cation organic solvents are tabulated. The sixth chapter entitled Raman measurements on flames by M. Lapp and C.M. Penny deals with the use of Raman spectroscopy as a probe for the determination of temperatures and densities of the main constituents of combustion systems.

Each review is accompanied by a comprehensive list of relevant literature references. The editors have recommended the use of SI units. A table containing the international system of units is given at the beginning of each volume. Author and subject indices covering all chapters are given at the end of each volume.

Majority of the articles appearing in this series are technique oriented and hence these volumes are extremely useful for chemists and biologists who want to apply infrared and Raman spectroscopy for solving problems of analysis, structure determination and quality control. They are also useful for physicists who are interested in solving fundamental problems. Beginners in Raman and infrared spectroscopy may find the subject matter contained in these volumes too advanced for their use.

R.S. KRISHNAN

X-RAY DIFFRACTION TOPOGRAPHY by B. K. Tanner (Heyden Publishers Ltd, London), 1976. Pp. xiv+ 125. Price £ 9·50; Rs 152

X-ray diffraction topography is now recognized as a versatile tool for non-destructive characterization of single crystals regarding perfection. This technique has been developed in the last 15 years or so. It can be used to characterize bulk crystals as large as several cm in diameter and a mm or so thick. In terms of resolution, this technique is not as powerful as electron microscopy. In an electron microscope, one can resolve dislocations even when their densities are very high. In X-ray topography, the limit is generally 10^5–10^6 per cm^2. This is 5–6 orders of magnitude smaller than attainable in electron microscopy. However, this advantage is offset considerably due to the capability of topography to characterize entire volume of big crystals, which is not possible with electron microscopy. Moreover, the present day crystal growth techniques produce crystals which are nearly perfect and contain low dislocation densities. In industry also, the requirement regarding perfection is quite stringent. The crystals to be used for device fabrication have dislocation densities of about a thousand per cm^2 or less than this. Single crystals of most of the semiconducting materials are practically free from line defects. X-ray diffraction topography has, therefore, been of great interest to industries, as well as to scientists engaged in fundamental research.

The work on topography dates back to 40's, when some of the initial experiments were performed by one of our leading scientists, Prof. G.N. Ramachandran. At this time, people used different approaches, for example, Guinner-Tennevin, or the method due to Berg-Barret. The pioneering work of A.R. Lang put this technique on a very firm footing. In the 70's work of Schwuttke and other scientists in industry demonstrated the great usefulness of this technique in applied work. Till now several review articles have been written about this technique. However, the present book by Tanner is the first monograph in this rapidly expanding area of research.

The book is divided into 7 chapters. The first chapter describes basic dynamical diffraction theory which is essential to understand the finer aspects of X-ray diffraction topography. In general, X-ray diffraction topography can be used in both pure kinematic and pure dynamic diffraction cases as well as in partly kinematic and partly dynamic diffraction cases. The essentials of the theory have been very briefly summarized in this chapter. In the second chapter, the author describes experimental techniques, including the most modern synchrotron topography and the topography system attached with an on-line TV monitor, which enables one to see the imperfections practically instantaneously. The author has briefly described the double crystal system and the basic principles of X-ray interferometry. The next two chapters are on characterization of defects and list the criteria used for this purpose. These chapters may be very useful for those who want to initiate research in this area. In the remaining three chapters, the author has described the results obtained on the characterization of single crystals grown by different techniques as well as single crystals obtained from natural sources. These are very illustrative and give a general idea of the degree of perfection and the types of defects which one encounters in crystals of different classes. Regarding vapour grown whisker crystals it is quite satisfactory to note that even though the bibliography is not very complete, the author has clearly stated the inadequacy of the screw dislocation theory to explain the growth of whiskers from vapour phase.

The book contains many beautiful topographs which have been reproduced very well. It is hoped that this book will serve the important purpose for those working in the area of X-ray topography and for those who want to start work in this area. The treatment of topics like X-ray interferometry is by no means exhaustive; however, the book provides a good introduction to it.

KRISHAN LAL

Notes & News

Possibility of neutrino telecommunication

During the past several years attempts have been made to utilize the enormous penetrating power of the neutrinos through matter to use them as ideal candidates for point-to-point direct line communication through the earth. At present global communication is accomplished by reflecting electromagnetic waves from the ionosphere or by retransmitting them by way of satellite relay. But neither elementary particles nor radio waves can pass through earth unhampered. The only limitation of the use of neutrino beam for such communication is the low intensity of the currently available neutrino beams.

Recent work of A.W. Saenz and his colleagues at the Naval Research Laboratories has led to revival of interest in neutrino beam communication. They have conducted a feasibility study and calculated several possible solutions. The principle of the proposed system is as follows. All along its path through water (an ocean or a lake, say), a neutrino beam produces charged particles (mostly muons and hadrons) that emit cerenkov radiation. Collected on clear plastic plates and monitored by strings of photo-sensitive detectors spaced some twenty meters apart, the cerenkov photon pulses could be translated into an intelligible code.

There might be two sources of background "noise" to this communication system, viz. sunlight and the cerenkov radiation of cosmic ray muons. The scientists at NAL suggest these can be sufficiently shielded by immersing the detection equipment at a depth of 400-500 m. It is further suggested that synchronous receiving techniques might be used to distinguish random background bombardments from the periodic 20 msec neutrino signal pulse.

Neutrino beams with energies of 200 GeV are now being produced at Fermi Lab outside of Chicago and within a year or two with the modifications planned for the proton accelerator these should be able to produce a beam of the order of 1000 GeV which is intense enough to attempt global communication. At present, attempts are being made to begin tests of neutrino telecommunications over modest distances—between Fermi Lab and Lake Michigan where the accelerator's beam is now directed [*Science*, **198** (1977), 295].

Nuclear matter distributions

The distribution of charge, and hence that of the protons in a nucleus, is known rather accurately for many nuclei from analyses of electron elastic scattering. But the neutron distribution cannot be found in the same way, because the nuclear force is not so well understood as the electromagnetic force.

To obviate this difficulty, the elastic scattering of very high energy ($\sim$1 GeV) protons from the nucleus is studied. Some new work on these lines has been reported by Blampied and coworkers [*Phys. Rev. Lett.*, **39** (1977), 1447]. They measured to very high accuracy the cross-sections for the elastic scattering of 800 MeV protons from ^{12}C, ^{58}Ni and ^{208}Pb using the high resolution spectrometer at the Clinton P. Anderson Meson Physics Facility at Los Alamos. The nucleon distribution was chosen to have a 3-parameter Fermi form with a Gaussian correction term. The formalism then allows the proton scattering cross-section to be calculated from any assumed nucleon distribution; the analysis then can proceed as in the case of electron scattering. It was found that the experimental data can be fitted very accurately, suggesting that the nucleon distribution is quite well determined. The parameters of the optimum nucleon distribution worked out by this team showed that the differences between the rms radii of the proton and neutron distribution in the nucleons are not significantly different from zero.

However, the use of parameterized nucleon distribution is known to introduce undesirable correlations between the densities at different radial distances, and it is preferable to use either an expression with no such correlations or a charge distribution with a more fundamental theoretical basis [*Nature. Lond.*, **272** (1978), 129].

Laser velocitimeter for aerosol wind speed measurement

The application of laser Doppler radar principle for measuring fluid flow and atmospheric wind speeds, i.e. laser doppler velocitimetry (LDV), is well known. However, LDV devices, especially the differential and cross-beam versions, are suitable for short-range forward scattered mode of operation only. This difficulty is overcome in a new type of dual beam back-scatter LDV device termed laser time of flight velocitimetry (LTV) designed at the Physics Department, Colorado State University, Colorado 80523, USA. It measures wind speeds in the atmosphere at remote points within a few hundred meters of the device, by measuring the time of flight of an aerosol particle across two parallel laser beams with a narrow separation.

The 6328 Å wavelength output from a helium neon laser is divided and focussed into two parallel beams with a close separation D. Both the beams are focussed by a telescope with aperture D_0 ($> D$) $\approx$ 6 cm into two intense and closely separated diffraction limited spots, in the remote observation region. The spots are monitored in the focal plane of a 2 cm receiving telescope. An aerosol particle which traverses across both the spots scatters two light pulses (i.e. beam scintillation) separated by time of aerosol flight, T, which is measured with the aid of a clipped digital corelator. The normal component of the wind speed $v_1 = D/T$. The aerosol particle back-scatters (at an angle α) the focussed spots in the region, at distance R metres away from the 2 cm receiving telescope. The resulting interference pattern in the focal plane determines D.

The advantage of the new LTV device is that it measures wind speed from correlation with the velocity of a single aerosol particle, unlike the previous LDV devices which make use of slightly un-

certain statistical correlations involving simultaneous motion of several aerosol particles. [*Optics Lett*, **1** (5) (1977), 175].

Device for detection of optical bistable state

Physicists at the Bell Telephone Laboratories, Murray-Hill, N.J. (USA) discovered in 1969 a new non-linear effect in optical media such as sodium vapour in a tuned Fabry Perot resonator through irradiation with intense laser beam, rendering the medium to be transformed back and forth from transparency to opaque. Known as 'optical bistability', the phenomenon exhibits a complete hysteresis cycle between the states of transparency and opacity. So far this effect has been observed primarily in media such as Na-vapour and ruby with a natural nonlinear refractive index profile. Now P.W. Smith and Edward Turner from Bell Labs at the Holmdel, N.J. have demonstrated the phenomenon termed hybrid bistability using the electrooptical crystal, potassium dihydrogen phosphate (KDP) with a feedback electrical network.

The KDP crystal is placed in the cavity of a Fabry Perot resonator in near resonance with the frequency of input focussed laser beam from a tunable (optical and infrared) dye laser. A beam splitter in the path of the output beam from the cavity sends a portion of the output onto a detector whose amplified output electrical signal is applied as feedback into two electrodes on two faces of the KDP crystal. The resulting electric field in the crystal, which is proportional to the input laser beam power, modulates the refractive index of the crystal. As a result of this, the KDP behaves as a bistable state medium, depending upon the input beam power. As the laser power is raised from a low value to a high value and then lowered, the KDP crystal (akin to sodium vapour medium) exhibits a complete hysterical cycle between opacity and transparency.

A quantum-optical theory of this effect, as a result of absorption and re-emission of light (photon) from a non-linear dispersive medium was proposed in 1976 both by workers at Bell Labs, Murray-Hill, N.J. and by Lugiato and Bunifacio of the University of Milan (Italy).

The new hybrid KDP device is a more efficient optical bistable device compared to the hitherto tried Na-vapour and ruby in that it responds to input powers (in a wide spectral band both optical and infrared) as low as 10^{-12} J, with switching times within a few nanoseconds (limited only by the detector sensitivity). Integrated devices based on optical bistability using crystals like lithium niobate have also been built. Such devices may find application in optical integrated circuit, in optical communication and optical computers. [*Physics Today*, **30** (12) (1977), 17].

Hypertension-causing gene identified

The portion of the gene that is at least partially responsible for high blood pressure that develops in rat fed on high salt diets has been identified at the Medical College of Ohio in Toledo.

The gene locus, designated Hyp-1, for hypertension, codes specifically for an enzyme that guides the synthesis of 18-hydroxydeoxycorticosteroid, a hormone similar to steroids known to induce hypertension in human beings.

The gene locus was identified in rats, known as the S-strain, which was found to develop abnormally high blood pressures (200–240 mm Hg) when fed a high-salt diet for eight weeks. In another strain of rats (R-strain), blood pressures remained low (120-140 mm Hg) on the same high salt diet. It is now known from classial genetic technique that S and R rats have identified differences at approximately two to four genetic loci which influences blood pressure.

On breeding the two strains together, about 10% of the blood pressure differences between them could be ascribed to the Hyp-1 locus. Work aimed at identifying the genetic loci responsible for the other 84% is in progress. Preliminary evidence suggests that some of the other gene loci may code for four proteins produced by the pituitary gland and which also may play a role in hypertension [*Chem. Engng News*, **56** (6) (1978), 23].

CALPHAD: Coupling of Phase Diagrams and Thermochemistry

This is a new international quarterly journal published by the *Pergamon Press Ltd*, Headington-Hill, Oxford OX3 OBW, U.K. with Prof. L. Kaufmann, *Manlabs Inc.*, Cambridge, Massachusetts, USA as the Editor-in-Chief. CALPHAD is a special project taken up in 1973 by a small group of practising thermodynamicists engaged in computer-based coupling of thermochemical and phase diagram data. The introduction of computer based methods for synthesizing the results of diverse thermochemical and phase diagram data has provided scope for assessing, collating and disseminating information which is important in many industrial processes. The journal forms part of such a dissemination program.

The inaugural issue (commenced 1977) covers mainly the work of CALPHAD group, and contains papers in the areas of metallic systems, ceramics, salt and inorganic materials, relations between thermochemical and phase diagram data, etc.

The annual subscription for institutional subscribers is US $ 64·00.

National Geophysical Research Institute, Hyderabad

According to the annual report of the institute for 1976-77, multidisciplinary efforts were made for the exploration and management of ground water, minerals, geothermal resources and investigation of the solid earth. During the year, the institute investigated 33 reseach projects under eleven broad areas. The financial inputs for 1976-77 amounted to Rs 115·337 lakh. The earnings from sponsored surveys, sale of instruments, consultation fee, etc. were about Rs 10·958 lakh.

Under the UNDP-aided project for development of improved geophysical techniques and instrumentation, work has been in progress to develop time domain IP equipment, bore-hole logging

equipment and a VHP radio beacon for automatic updating of airborne position location system. The results of the research on well-logging techniques have indicated that response of 'Lateral and Laterolog 7' devices can be synthesized from 'normal' or 'two-electrode' response. Problems in transient EM sounding over (i) multi-layered earth cross-section under cover of a conducting overburden, and (ii) 3-layered earth with conductive/resistive intermediate layer have been studied.

Experimental resistivity surveys were carried out to locate the boundary of waterlogged old and abandoned mines in Raniganj coalfields. Resistivity surveys were also carried out on Nhava Island off Bombay coast for determining the thickness of top soil and depth of the bedrock.

The institute has successfully designed and built an inverter power supply for improving the performance of the rubidium vapour magnetometer developed earlier. A device to quantitatively estimate the reflectance of iron ore dust samples has been fabricated. The device will be useful for the friability estimation of iron ores.

The first phase of integrated geohydrological studies in the Lower Maner Basin has been completed. Resistivity prospecting for groundwater in some drought-prone areas of Uttar Pradesh was carried out. Resistivity surveys have also been carried out in a 1700 sq km area of Mahanadi delta to delineate aquifers and outline saline/fresh water boundaries.

Simulation studies for groundwater management were continued. An R-C analog modelling study of aquifer systems in Krishni-Hindon interstream region was carried out using the hydrogeological data procured from the Bhabha Atomic Research Centre, Bombay. The study has indicated that the aquifer cannot sustain the present heavy withdrawal of groundwater and over the next five years the water level will further decline.

Sponsored geophysical surveys for groundwater have been carried out in different parts of Andhra Pradesh and the union territories of Goa, Daman and Diu. About 170 villages have been covered since January 1975 in this region. Altogether, 350 points have been recommended for tapping groundwater through bore-wells, or dug-wells or bore-cum-dug wells. Most of the dug- or bore-wells completed have proved to be successful. Bedrock investigations have been undertaken for Buggavanka reservoir scheme across Buggavanka river near Cuddapah, at the proposed dam site for Peddaru reservoir scheme near Madanapally and for Krishnapuram reservoir scheme near Karvetinagar in Chittoor Dist. at the request of the Government of Andhra Pradesh.

Under deep seismic sounding (DSS) project, the activities extended from analyses and interpretation of DSS data obtained in Peninsular Shield and Pamir-Himalaya to shooting of fresh DSS profiles in the states of Gujarat and Maharashtra.

Preliminary depth sections along 7 sub-profiles have been obtained using reflected/refracted arrivals in Koyna area and Deccan traps along Guhagar-Jath profile. Average and interval velocity functions have been obtained from Deccan trap region of Maharashtra and effective velocity and depth nomograms developed. These will be employed to construct a final depth section along Guhagar-Jath profile.

At the request of the Oil & Natural Gas Commission (ONGC) DSS field work was carried out along a 200 km long profile running between Mahmedabad and Navasari in Gujarat. It is the first time that DSS studies are being used in a sedimentary basin to obtain deep geological information required in oil exploration programmes. Wide angle reflections have been recorded all along the profile besides clear vertical reflections, at various shot points, from horizons occurring at depths of 1 to 12 km.

DSS work was also carried out in Gujarat along a 160 km long profile from Navibandar to Amreli. Besides recording wide angle reflections, clear vertical reflections were recorded at various shot points.

Studies on geothermal resources along the western coast were continued. These comprise hot springs of Konkan, Tural-Rajwadi and Unhavare (Khed) areas. It has been observed that 27 hot springs have temperatures of 27-58°C in Akloli-Ganeshpuri area of Thana district (Maharashtra) and a cluster of eleven hot springs with temperature ranging from 41° to 61°C occur in Tural-Rajwadi area and one hot spring has a temperature of 7·0°C in Unhavare (Khed) hot spring area. These geothermal waters have been analysed chemically. Thermal investigations have been carried out in Manikaran-Kasol-Jan hot spring areas and Vashisth-Kalath hot spring area of Kulu valley.

Thermal logging of 10 boreholes in various geological provinces of India has been carried out.

Paleomagnetic studies were carried out to understand the movement of Indian Plate and various tectonic phases of Himalayan orogeny. Paleomagnetic studies have also been undertaken in Peninsular shield. In this connection, a large number of oriental samples were collected from a number of formations. Physical and elastic properties of rocks under NTP and their behaviour under high temperatures and pressures have also been studied.

Integrated geological, geochemical and geophysical studies have been undertaken in certain critical areas of the Himalayas and Peninsular India.

Geophysical data were regularly recorded in the observations of NGRI and exchanged with other data centres for global study.

Thirty-three research papers and 17 technical reports were published during the year.

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